# Radiation Technology for Polymers



## Jiri George Drobny

# Radiation Technology for Polymers

SECOND EDITION

# Radiation Technology for Polymers

Jiri George Drobny

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*To Betty Anne*

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# *Preface to the First Edition*

The industrial use of ultraviolet (UV) and electron beam (EB) radiation is growing at a fast pace and is penetrating many areas, such as electronics, automotive, printing, adhesives and coatings, packaging, etc., which traditionally have had their own well-established processes. Information on this topic useful to a professional can be found in many places, such as encyclopedias (*Encyclopedia of Polymer Science and Engineering*, *Ullmann's Encyclopedia of Industrial Chemistry*), professional publications (*PCI*, *Paint and Coating Industry*, *Paint & Powder*, *FLEXO*, *Converting*, *Modern Plastics*, *Rubber Chemistry and Technology*, *Modern Plastics*, *Wire and Cable*, *Radiation Physics and Chemistry*, *Journal of Applied Polymer Science*), and others. RadTech News, a publication of RadTech North America, covers applications, new technology, and industry news. During the past few years, several very informative books have been published by SITA Technology Ltd. in the UK that cover different aspects of UV/EB radiation technology in great detail. However, seeking specific information may be prohibitively time-consuming and a need for a quick reference book is obvious.

*Radiation Technology for Polymers* is designed to meet this need by providing systematic fundamental information about practical aspects of UV/EB radiation to professionals in many different fields. The intended audiences are mainly chemists or chemical engineers new to UV/EB radiation technology. Another reader of this book may be a product or process designer looking for specifics about the effects of UV/EB on a specific polymeric material or for a potential technological tool. This book may also be a useful resource for recent college and university graduates or for graduate or undergraduate students in polymer science and engineering and for corporate training. Because of the breadth of the field and the multitude of applications, the book does not go into details; this is left to publications of a much larger size and scope and to professional periodicals. Rather, it covers the essentials and points the reader toward sources of more specific and/or detailed information. *Radiation Technology for Polymers* is not a competition to other books on the subject, it merely complements them. With this in mind, this book is divided into eleven separate chapters, covering the principles of generating UV and EB energy, equipment, processes, applications, dosimetry, safety, and hygiene. The last chapter covers the newest developments and trends.

This book began as lectures and seminars at the Plastics Engineering Department of the University of Massachusetts at Lowell and to varied professional groups and companies in the United States and abroad. It draws from the author's more than 40 years of experience as an R&D and manufacturing professional in the polymer processing industry and more recently as an independent international consultant.

My thanks are due to the team from the CRC Press, Susan Farmer, Helena Redshaw, and Sylvia Wood, for helping to bring this work to fruition; to my family for continuing support; and Dr. Ewa Andrzejewska, John Chrusciel, Dr. Joseph Koleske, and Richard W. Stowe for valuable comments and recommendations.

*Merrimack, New Hampshire*
*April 2002*

# Preface to Second Edition

The first edition of *Radiation Technology for Polymers* had the main goal of providing systematic fundamental information to professionals entering the industrial practice of radiation technology as it applies to processing of polymers or already working in this field. Since its publication in 2003 the industry has changed markedly. Many technological developments have taken place, new applications and products have been developed and commercialized, and some already established ones were discontinued. Companies were sold and bought, reorganized, or renamed. UV/EB technology is becoming increasingly more important in a variety of issues, such as its continuing quest for further reduction of volatile organic compounds and toxic substances in the environment, development of alternative sources of energy, and more. Thus, it was time to update the publication to include these changes, developments, and issues. As the first edition, the second edition still stresses the practical aspects of UV/EB technology and its industrial applications. Few illustrations were added, and one of the major features is the addition of processing and engineering data of some commercial products. In addition, the feedback from colleagues, students, clients, and attendants of various seminars and training sessions was helpful in preparing the manuscript of this updated and expanded edition.

Special thanks go to Anthony J. Berejka, Dr. Marshall R. Cleland, and Richard W. Stowe for editing parts of the manuscript and providing helpful comments and recommendations.

Allison Shatkin, who was very helpful and encouraging from the beginning until the end of the preparation of the manuscript, deserves many thanks. A special credit is due to the team from CRC Press, particularly to Andrea Dale, Jennifer Ahringer, and Amy Rodriguez, for bringing this work to fruition.

**Jiri George Drobny**
*Merrimack, New Hampshire, and Prague, Czech Republic*
*June 2009*

# *About the Author*

**Jiri George Drobny** was educated at the Technical University in Prague in chemical engineering, specializing in processing of plastics and elastomers, and at the Institute of Polymer Science of the University of Akron (Ohio) in physics and engineering of polymers. He also earned an MBA in finance and management at Shippensburg State University in Shippensburg, Pennsylvania. His career spans over 40 years in the rubber and plastics processing industries in Europe, the United States, and Canada, mainly in R&D with senior and executive responsibilities. Currently, he is president of Drobny Polymer Associates, an international consulting firm specializing in fluoropolymer science and technology, radiation processing, and elastomer technology. Drobny is also active as an educator, author, and technical and scientific translator. He is a member of the Society of Plastic Engineers, American Chemical Society, and RadTech International North America, and is listed in *Who's Who in America*, *Who's Who in Science and Engineering*, *Who's Who in Plastics and Engineering*, and *Who's Who in the East*. He resides in New Hampshire.
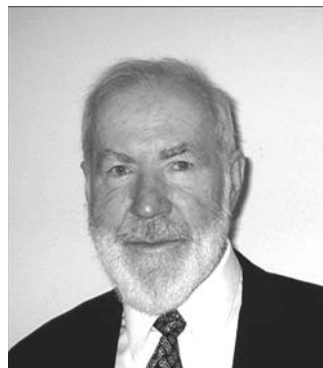
# 1

## *Introduction*

Radiant energy is one of the most abundant forms of energy available to mankind. Nature provides sunlight, the type of radiation that is essential for many forms of life and growth. There are some natural substances, which generate yet another kind of radiation that can be destructive to life, but when harnessed it can provide other forms of energy or serve in medicine or industrial applications.

Human genius created its own devices for generating radiant energy useful in a great variety of scientific, industrial, and medical applications. Cathode ray tubes emit impulses that activate screens of computer monitors and televisions. X-rays are used not only as a diagnostic tool in medicine, but also as an analytical tool in inspection of manufactured products such as tires and other composite structures. Microwaves are used not only in cooking or as means of heating rubber or plastics, but also in a variety of electronic applications. Infrared radiation is used in heating, analytical chemistry, and electronics. Manmade ultraviolet radiation has been in use for decades in medical applications, analytical chemistry, and in a variety of industrial applications. Devices used to generate accelerated particles are not only valuable scientific tools, but also important sources of ionizing radiation for industrial applications. Both ultraviolet (UV) and electron beam (EB) radiations are classified as electromagnetic radiations, along with infrared (IR) and microwave (MW). The differences between them in frequency and wavelength are in Table 1.1.

Polymeric substances, which are predominantly high-molecular-weight organic compounds, such as plastics and elastomers (rubber), respond to radiation in several ways. They may be gradually destroyed by UV radiation from sunshine when exposed for extended periods of time outdoors; they may more or less change their properties. On the other hand, manmade UV radiation is actually used to produce polymers from monomers (low-molecular-weight building blocks for polymers) or from oligomers (essentially very low-molecular-weight polymers). In these reactions, almost always a liquid is converted into a solid almost instantaneously. Ionizing radiation (γ-rays and high-energy electrons) is even more versatile: it is capable of converting monomeric and oligomeric liquids into solids, but also can produce major changes in properties of solid polymers.

**TABLE 1.1**

Frequency and Wavelength of Various Types of Electromagnetic Radiation

| Radiation | Wavelength, μm | Frequency, Hz |
|---|---|---|
| Infrared | $1-10^2$ | $10^{15}-10^{12}$ |
| Ultraviolet | $10^2-1$ | $10^{17}-10^{15}$ |
| Microwave | $10^3-10^5$ | $10^{12}-10^{10}$ |
| Electron beam | $10^{-7}-10^{-4}$ | $10^{21}-10^{18}$ |

*Source:* This article was published in Datta, S., Chaki, T. K., and Bhowmick, A. K., in *Advanced Polymer Processing Operations* (Cheremisinoff, N. P., Ed.), Noyes Publications, Westwood, NJ, Chapter 7, p. 158 (1998). Used with permission from Elsevier Ltd.

## 1.1  Basic Concepts

Industrial applications involving radiation processing of monomeric, oligomeric, and polymeric substances depend essentially on two electrically generated sources of radiation: accelerated electrons and photons from high-intensity ultraviolet lamps. The difference between these two is that accelerated electrons can penetrate matter, and are stopped only by mass, whereas high-intensity UV light affects only surface.[1] Generally, processing of monomers, oligomers, and polymers by irradiation by UV light and electron beam is referred to as *curing*. This term encompasses chemical reactions including polymerization, cross-linking, surface modification, and grafting. These reactions will be discussed in detail in the appropriate chapters.

The process of conversion of liquid to solid is mainly designed to use on compositions based on nonvolatile monomers and oligomers with molecular weights of less than 10,000. These have low enough viscosities, so that they can be applied without the use of volatile solvents (volatile organic compounds [VOCs]).[1] This, of course, is greatly beneficial for the environment, more specifically, the air. In fact, some states have recognized UV/EB curing of coatings, printing inks, paints, and adhesives as environmentally friendly in their legislative actions.[1] For example, when the EB process is compared to solvent-based coatings and even to water-based technology, another "green" alternative to VOC-based technology, it is found to be far superior in energy consumption (see Table 1.2). Moreover, the UV/EB technology is superior to solvent-based systems concerning greenhouse gas emissions. Thus, the amount of $CO_2$ from solvent combustion, typically 37 g/m³, generates a facility emission potential of 415.8 kg/h.[2]

Clearly, UV and EB radiation have a great deal in common, as shown above. However, there are also differences. Besides the nature of interacting with matter, where high-energy electrons penetrate, and photons cause only surface effects, there are issues concerning the capital investment and chemistry involved.

Without any doubt, the UV irradiation process is the lower-cost option, since the equipment is simpler, smaller, and considerably less expensive to

**TABLE 1.2**

Energy Needed to Dry/Cure Coatings

| Property/Energy | System | | |
|---|---|---|---|
| | **Solvent** | **Water** | **EB Curable** |
| Solids, weight % | 40 | 40 | 100 |
| Diluent | Toluene | Water | None |
| Boiling point, °C | 111 | 100 | N.A. |
| Vapor pressure, mmHg (20°C) | 22 | 17 | N.A. |
| Energy to dry/cure, 1 g dried coating, J/g | 555 | 3,390 | 30 |

purchase and operate. Normally, there is no need to used nitrogen inerting, which adds to operating expenses. However, free-radical-based UV curing requires the addition of photoinitiators, some of which are expensive and may bring about some undesirable effects, such as discoloring of the film and often also odor. Both these effects can be minimized or eliminated by nitrogen blanketing.[3] It is much more difficult to cure pigmented films, particularly thick ones using UV irradiation, while these can be cured without problems by electron beams. Photoinitiator and sensitizer residues from UV cured formulations may migrate and render some products, such as food packaging, unacceptable. In most cases this problem does not exist with EB cured products. Coatings formed from similar formulations but cured with UV or EB radiation may differ in their physical properties, such as scratch resistance and swelling resistance. This is conceivable, since the two processes are fundamentally different.[4]

Organic molecules become electronically excited or ionized after absorption of energy. For the transformation of organic molecules from the ground state to the excited state, energies typically in the range from 2 to 8 electronvolts (eV) are required.[5] The excited molecules are able to enter into chemical reactions leading to chemically reactive products that initiate the polymerization, cross-linking, and grafting reactions.

Ionization of organic molecules requires higher energy. The ionization process generates positive ions and secondary electrons. When reacting with suitable monomers (e.g., acrylates), positive ions are transformed into free radicals. Secondary electrons lose their excess energy, become thermalized, and add to the monomer. The radical anions formed this way are a further source of radicals capable of inducing a fast transformation.[5]

In industrial irradiation processes, either UV photons with energies between 2.2 and 7.0 eV or accelerated electrons with energies between 100 and 300 eV are used. Fast electrons transfer their energy to the molecules of the reactive substance (liquid or solid) during a series of electrostatic interactions with the outer sphere electrons of the neighboring molecules. This

leads to excitation and ionization, and finally to the formation of chemically reactive species.[5] Photons, on the other hand, are absorbed by the chromophoric site of a molecule in a single event. In UV curing applications special photoinitiators are used, which absorb photons and generate radicals or protons. The fast transformation from liquid to solid can occur by free radical or cationic polymerization, which in most cases is combined with cross-linking. In liquid media, the transformation takes typically 1/100 of a second to 1 s. However, in rigid polymeric matrix free radicals or cationic species last longer than a few seconds. A post- or dark cure process proceeds after irradiation, and the result is a solid polymer network.[5]

In summary, UV and electron beam technology improves productivity, speeds up production, lowers cost, and makes new and often better products. At the same time, it uses less energy, drastically reduces polluting emissions, and eliminates flammable and polluting solvents.

The technology is widely used to protect, decorate, or bond items, including fiber optics, compact discs, DVDs, credit cards, packaging, magazine covers, medical devices, automotive parts, aerospace products, and more.

## References

1. Berejka, A. J., in *Proceedings 3rd Annual Green Chemistry and Engineering Conference: Moving Toward Industrial Ecology* (June 29–July 1, Washington, DC), p. 35 (1999).
2. Berejka, A. J., *RadTech Report*, 17, No. 5, September/October, p. 47 (2003).
3. Datta, S., Chaki, T. K., and Bhowmick, A. K., in *Advanced Polymer Processing Operations* (Cheremisinoff, N. P., Ed.), Noyes Publications, Westwood, NJ, Chapter 7, p. 158 (1998).
4. Davidson, R. S., *Exploring the Science, Technology, and Applications of U.V. and E.B. Curing*, SITA Technology Ltd., London, p. 27 (1999).
5. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 1 (1998).

# 2

## Review of Radiation Science and Technology

### 2.1 UV and Visible Radiation

*Ultraviolet radiation* is part of the electromagnetic spectrum and shows wavelength in the range from 40 to 400 nm. It is known as *nonionizing* or *actinic* radiation. Ultraviolet radiation is divided into the following four regions:[1]

Vacuum UV (VUV): 40–200 nm

UV C: 200–280 nm

UV B: 280–315 nm

UV A: 315–400 nm

Vacuum UV (VUV) is strongly absorbed by quartz, which is used as the envelope material for bulbs. Because of that and because of its small penetration depth, VUV is not suitable for usual radiation curing.

The radiation with wavelengths between 400 and 760 nm is *visible light*, which is useful and even advantageous for certain applications.[2] The energy from visible light is less powerful than that from ultraviolet radiation sources, and consequently, curing times are longer. Another advantage of visible light is that there is less scatter of the longer wavelengths than of those in the UV range, and therefore greater depth of cure can be achieved.[3]

UV energy can be generated by the use of either *electric current* or *microwave energy*. In the first method, the current is passed through a sealed quartz envelope (bulb) having an electrode on each end. It creates an arc across the electrodes, which vaporizes the fill of the bulb (typically mercury) and creates plasma. In the second method, the quartz bulb does not have electrodes and the power is supplied by magnetrons, creating a microwave field around the bulb. Mercury inside the bulb reacts with the microwave energy and also creates *plasma*. In both cases, the plasma operates at about 6,000 K, which generates UV energy.[4]

Plasma is essentially an ionized gas, consisting of a mixture of interacting positive ions, electrons, neutral atoms, or molecules in the ground state or any higher state of any form of excitation as well as photons. Since charge

carrier pairs are generated by ionization, the plasma as a whole remains electrically neutral.[5]

Plasma is generated by energy transfer to a system of atoms or molecules until a gas phase is formed and high degree of ionization is achieved. In the sources of polychromatic UV light plasma is formed using mercury vapor, the source of energy is electricity, and the discharges in mercury vapor are excited by AC or DC, radio frequency, or microwave energy. Mercury is suitable as the fill gas for this process because of its relatively low ionization potential and sufficient vapor pressure in the range of temperatures used. Moreover, it is chemically inert toward the electrode and wall materials and has a favorable emission spectrum. The excited levels of the mercury atoms are high enough to allow excitation transfer to other metals, such as iron, gallium, lead, cobalt, etc., which allows the modification of the spectral output of the light source.[6]

In industrial applications, photons with energies ranging from 2.2 to 7.0 eV are used. The mercury discharge, as used in mercury arc lamps, produces a polychromatic spectrum with intensive emission lines ranging in energy levels from 2.8 to 6.0 eV.[7]

Monochromatic UV radiation is emitted by excimer lamps. In excimer lamps, microwave discharge[8] or a radio-frequency-driven silent discharge[9] generates excimer excited states of noble gas halide molecules, which decay by the emission of monochromatic UV radiation. Currently, excimer emissions from XeCl with wavelength 308 nm and energy of 4.02 eV and from KrCl with wavelength 222 nm and energy of 5.58 eV reach power levels required for fast cure speeds. Radiation from CuBr excimer with wavelength 535 nm and energy of 2.2 eV allows visible light curing. The emission from $Xe_2$ excimer with wavelength 172 nm and energy of 7 eV is used for special surface cure applications.[7]

### 2.1.1  Light Emission from Mercury Gas Discharge

UV light emission from mercury gas discharge with sufficient intensity results from self-sustaining discharges, such as glow and arc discharge. The glow discharge occurring at mercury vapor pressures of about $10^{-2}$ mbar and current in the range of 0.01 to 0.1 A (referred to as *abnormal glow*) produces emission of strong 185 and 254 nm radiation. The low-pressure mercury lamps operate in this region.[6] A typical arc discharge occurs at mercury vapor pressures from 0.1 to 10 bar and currents up to 10 A. Medium-pressure mercury lamps operate in the region of arc discharge with the most intensive transition at 365 nm, while various emission lines and some background radiation appear in the UV and visible ranges of the spectrum.[6]

Conventional mercury lamps are essentially sealed quartz tubes with tungsten electrodes at either end and filled with mercury metal and vapor and a starter gas (usually argon). When a high voltage is applied across the electrodes, the starter gas is ionized:

$Ar \rightarrow Ar^+ + e^-$       Ionization

$Ar^+ + e^- \rightarrow Ar^*$      Excitation

$Ar^*$ Excited state of argon
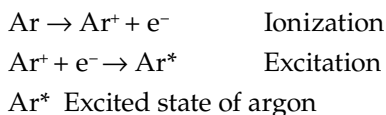
Recombination of the ionized electron with the argon cation produces an electronically excited argon atom, which can energize and subsequently ionize a mercury atom:

$Ar^* + Hg \rightarrow Hg^+ + e^-$

$Hg^+ + e^- \rightarrow Hg^*$

$Hg^*$ Excited state of mercury
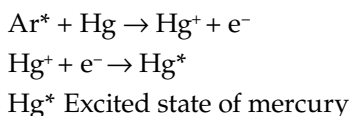
The electronically excited mercury atom generated by the recombination of the mercury cation with an electron loses its energy radiatively. The above are only a few of the processes that take place in the lamp, but the combined effect is the emission of light in the UV and visible regions and the generation of heat.[10] The heat vaporizes some of the mercury metal. The mercury cations are conducting and the current passing across the electrodes rises until a steady state is reached.

The spectral output of the mercury gas discharge matches the absorption spectra of many photoinitiators well; however, there are regions where more radiant power is required for specific application. An example is pigmented systems, where the pigment absorbs strongly at wavelengths below 360 nm. To generate required transitions, metal halides, such as gallium and iron halides, are added to the mercury discharge. Gallium addition produces strong spectral lines at 403 and 418 nm. Iron addition generates strong multiline emission between 350 and 400 nm.[11] Spectral outputs of some metal halide lamps compared to that of a standard mercury lamp are in Figure 2.1.

### 2.1.2 Light Emission from a Microwave-Excited Discharge

Microwave radiation, generated by a magnetron, can be directly transmitted to a quartz tube containing argon as a start gas and a certain amount of liquid mercury. The microwave energy produces a strong electric field inside the bulb, which ionizes argon. At the same time, the mercury is heated up and vaporized and becomes excited and to some extent ionized. Mercury vapor plasma is formed, which can operate at mercury pressures up to 20 bar (290 psi).[11] Spectral outputs of commercial microwave-driven lamps are shown in Figure 2.2.

### 2.1.3 Generation of Monochromatic UV Radiation

Excimer and nitrogen lasers are sources of pulsed monochromatic UV radiation with a variety of interesting wavelengths and high-output peak powers.
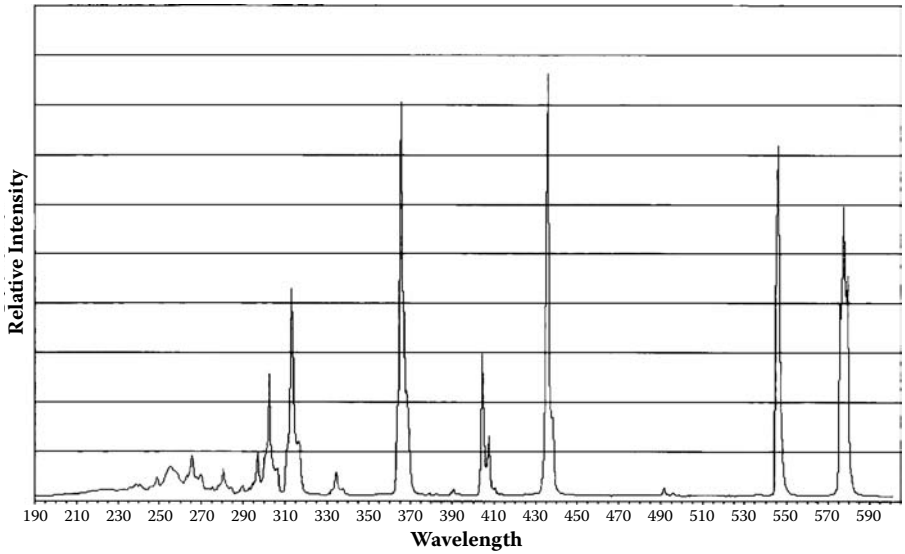
(a)
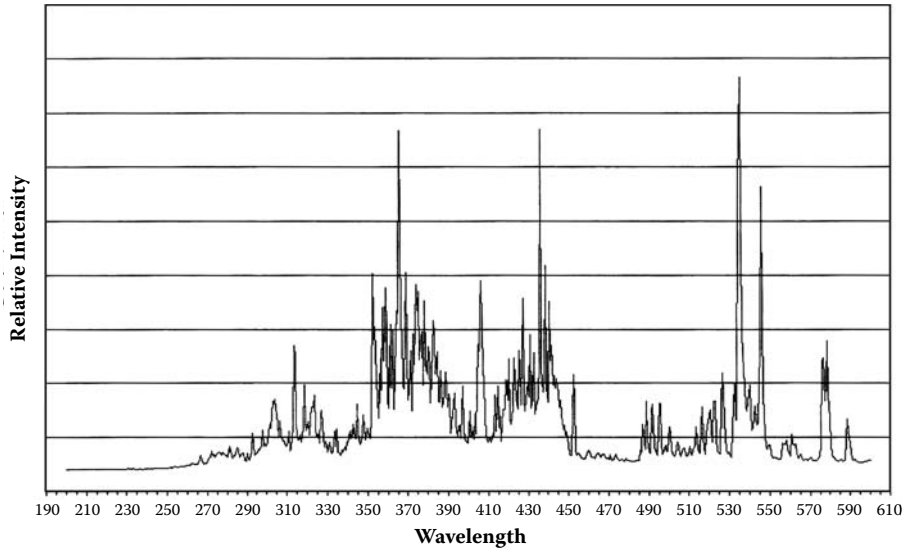


(b)

**FIGURE 2.1**
Spectral outputs of some typical metal halide lamps compared to that of the standard mercury lamp mercury barrier discharge lamp: (a) mercury barrier discharge lamp, (b) iron additive lamp, and (c) gallium additive lamp. (Courtesy of American Ultraviolet Company.)

(c)
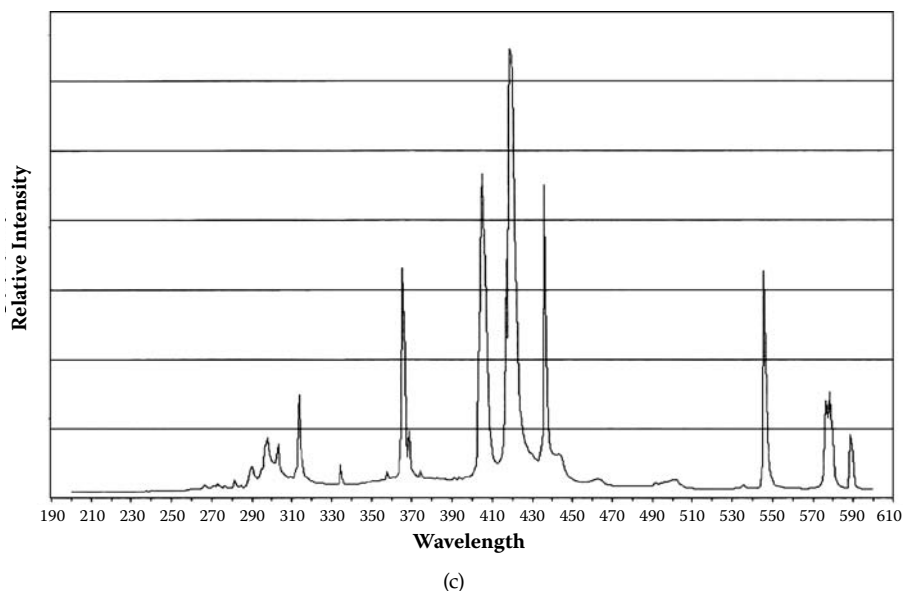
**FIGURE 2.1**
(Continued)

However, they cannot compete with mercury arc lamps in large-area, fast-cure applications because of their low pulse repetition rates.[12]

Excimer lamps, a relatively recent new development, represent a new class of monochromatic UV sources.[13] Excimers (excited dimers, trimers) are weakly bound excited states of molecules that do not possess a stable molecular state.[14]

The term stands for an electronically activated molecule in the gas phase consisting of two atoms. The formation process is the same as in lasers:[13]

1. Excitation of atoms in the gas phase within an electrical discharge:

$$A \rightarrow A^*$$

2. Formation of excimer molecules:

$$A^* + B \rightarrow AB^*$$
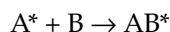
3. Decomposition of excimer molecules and generation of photons:

$$AB^* \rightarrow A + B + h\nu$$

   where h is the Planck's constant and $\nu$ the frequency of the photon emitted.
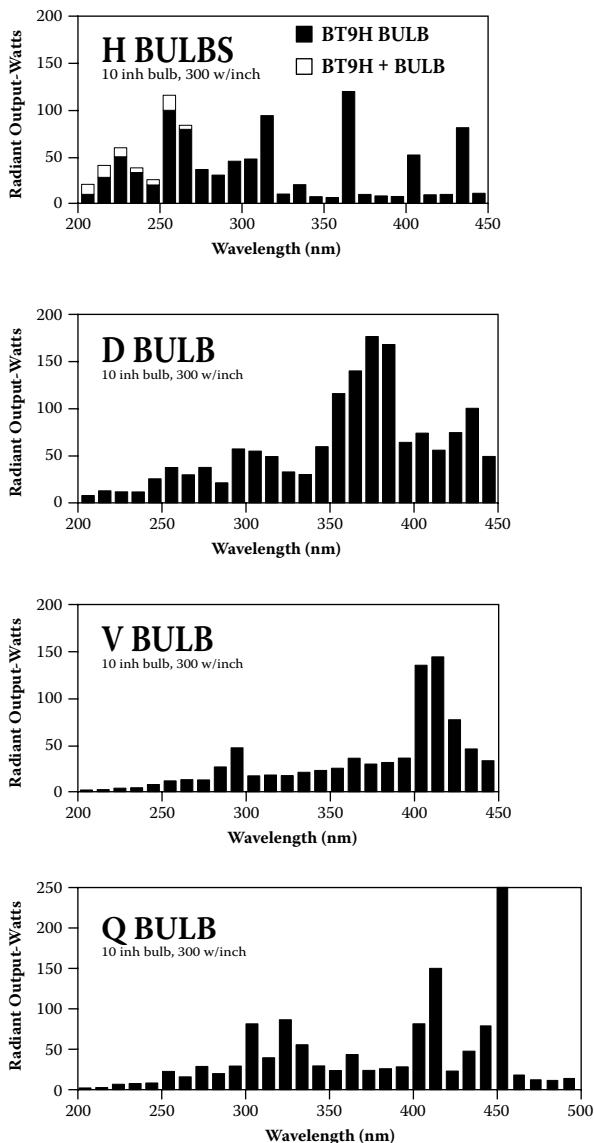
**FIGURE 2.2**
Spectral output of commercial microwave-driven lamps. (Courtesy of UV Fusion Systems.)

The wavelength of the emitted light depends on the choice of atoms A and B. Besides the principle of excimer formation, the technical parameters for the lamp and discharge are responsible for the quasi-monochromatic character of the emitted spectrum.[13] The most important commercial excimers are formed by electronic excitation of molecules of rare gases (He$_2$, Ne$_2$, Ar$_2$, Kr$_2$, Xe$_2$),

rare-gas halides (e.g., ArF, KrF, XeCl, XeF), halogens, and mercury halogen mixtures (HgCl, HgBr, HgI). They are unstable and decay by spontaneous optical emission. The peak maximum is at 308 nm with a half peak full width of about 5 nm.[14] Dielectric barrier "silent" discharges[9] or microwave discharges[8] can be used to produce quasi-stationary or continuous incoherent excimer radiation.

Excimers as radiation sources have the following characteristics:[15]

- They are very efficient energy converters. Theoretically, 40–50% of the energy deposited by electrons can be converted to radiation.[9,16]
- Due to absence of a stable ground state, no self-absorption of the excimer radiation can occur.
- In most cases, low-pressure excimer UV sources show a dominant narrow-band (1–3 nm) transition. They can be considered to be quasi-monochromatic.
- Excimer systems can be pumped with very high-power densities. Consequently, extremely bright UV sources can be built.

For industrial applications of excimer UV sources, the dielectric barrier and the microwave discharge are simple, reliable, and efficient excitation modes. There are a large number of vacuum UV (VUV), UV, and visible light transitions available. This allows a selective photoexcitation for many systems.[15] Some sources of monochromatic UV light for industrial applications and their characteristics are in Table 2.1.

## 2.2 Ionizing Radiation

As pointed out in Chapter 1, ionizing radiation includes high-energy electrons (electron beam), γ-rays, and x-rays. These not only are capable of converting monomeric and oligomeric liquids into solids, but also can produce major changes in properties of solid polymers. Also, in comparison to UV and visible radiation, they can penetrate considerably deeper into the material.

### 2.2.1 Electron Beam Energy

In principle, fast electrons are generated in a high vacuum (typically $10^{-6}$ torr) by a heated cathode. The electrons emitted from the cathode are then accelerated in an electrostatic field applied between cathode and anode. The acceleration takes place from the cathode that is on a negative high-voltage potential to the grounded vessel as anode. The accelerated electrons may sometimes be focused by an optical system to the window plane of the accelerator.[16]

**TABLE 2.1**
Monochromatic UV Sources for Industrial Applications

| Source | Emission Generated By | Main Emission Wavelengths, nm | UV Radiant Power, W/cm | Main Applications | Note |
|---|---|---|---|---|---|
| Low-pressure mercury lamp | Low-pressure glow discharge | 254 and 185 | 0.1–1.0 | Liquid crystal displays, photoresist technology | Weaker emission lines at 313 and 578 nm |
| Excimer lamp | Dielectric barrier (silent) discharge | 172, 222, 308 | 1–10 | UV curing, pollution control, surface modification | Major R&D efforts to increase the radiant power |
| | Microwave discharge  Low pressure | 222, 308 | 1–5 | | |
| | High pressure | | 12–64 | | |

The energy gain of the electrons is proportional to the accelerating voltage and is expressed in electron volts (eV), which represents the energy gained by a particle of unit charge by passing the potential difference of 1 V. The electrons leave the vacuum chamber only if their energy is high enough to penetrate the 15–20 µm thick titanium window of the accelerator. Details about the equipment used to produce electron beam are in Chapter 3.

When an electron beam enters a material (this includes the accelerator exit window, the air gap, and the material being irradiated), the energy of the accelerated electrons is greatly altered. They lose their energy and slow down almost continuously as a result of a large number of interactions each with only small energy loss.

Electrons, as any other charged particles, transfer their energy to the material, and through that they pass in two types of interaction:

- In collisions with electrons of an atom, resulting in material ionization and excitation.

- In interaction with atomic nuclei, leading to the emission of x-ray photons. This is referred to as *bremsstrahlung* (from German, meaning "breaking radiation"), an electromagnetic radiation emitted when a charged particle changes its velocity—slows down—due to such interaction.

Somewhat simplified, the process of interaction of high-energy electrons with organic matter can be divided into three primary events:

1. *Ionization*: Ionization takes place only when the transferred energy during the interaction is higher than the bonding energy of the bonding electron:

$$AB \rightarrow AB^+ + e^-$$

   At almost the same time, the ionized molecule dissociates into a free radical and a radical ion:

$$AB^+ \rightarrow AB\bullet + \bullet B^+$$

2. *Excitation*: Excitation moves the molecule from the ground state to the excited state:
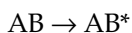
$$AB \rightarrow AB^*$$

   The excited molecule eventually dissociates into free radicals:

$$AB^* \rightarrow A\bullet + B\bullet$$
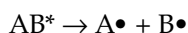
3. *Capture of electron*: This process is also ionization. Electrons with a still lower energy can be captured by molecules. The resulting ion can dissociate into a free radical and a radical ion:

$$AB + e^- \rightarrow AB^-$$

$$AB^- \rightarrow A\bullet + \bullet B^-$$
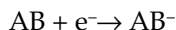
Besides these primary reactions, various secondary reactions take place in which ions or excited molecules participate. The final result of these three events is that, through the diverse primary and secondary fragmentations, radicals are formed and the complete cascade of reactions triggered by the primary excitation of molecules may take up to several seconds. The energy deposited does not always cause change in the precise position where it was originally deposited, and it can migrate and affect the product yield considerably.

The primary effect of any ionizing radiation is based on its ability to excite and ionize molecules, and this leads to the formation of free radicals, which then initiate reactions such as polymerization and cross-linking or degradation. Accelerated electron beams have energy sufficient to affect the electrons in the atom shell, but not its nucleus, and can therefore only initiate chemical reactions. Typically, the reactions initiated by electron beam are extremely fast and are completed in fractions of a second.

Electrons that are capable of electronically exciting and ionizing organic molecules, such as acrylates, epoxies, etc., must have energies in the range from 5 to 10 eV. Such electrons can be produced from fast electrons by the energy degradation process in solids, liquids, and gases. These secondary electrons show energy distribution with the maximum in the range from 50 to 100 eV. In contrast to fast electrons, exhibiting energies in the keV and MeV range, secondary electrons are capable of penetrating solids and liquids only a few nanometers. Consequently, they generate ions, radicals, and excited molecules in "droplets" along the paths of the fast electrons. Samuel and Magee denoted such droplets containing several pairs of ions, radicals, and excited molecules as "spurs."[17] Chemical processing by electron beam involving polymerization and cross-linking of monomers and oligomers, and cross-linking, modifications, grafting, and degradation of polymers are induced by different reactive species formed initially by electrons in the spurs.[18–20] Figure 2.3 illustrates schematically the process of generation of reactive species.[21]

Radiation processing with electron beam offers several distinct advantages when compared to other radiation sources, particularly γ-rays and x-rays:

- The process is very fast, clean, and can be controlled with a great deal of precision.
- There is no permanent radioactivity since the machine can be switched off.
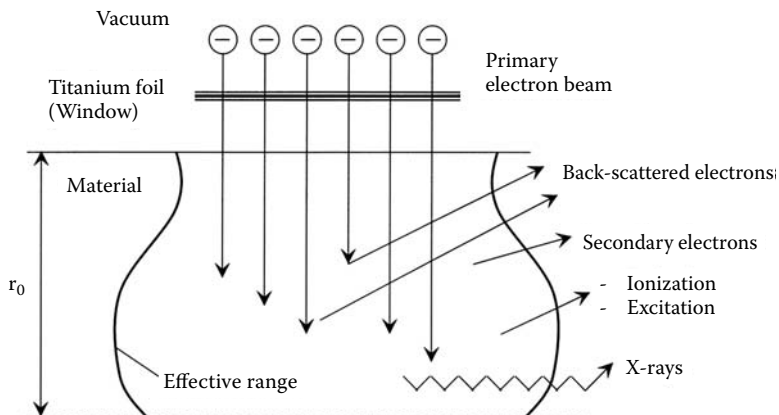
**FIGURE 2.3**
The process of generation of reactive species by high-energy electrons. (Garratt, P. G., *Strahlenhärtung*, Curt R. Vincentz Verlag, Hannover, p. 61 (1996). In German. Reprinted with permission from Vincentz Network.)

- In contrast to γ-rays and x-rays, the electron beam can be steered relatively easily, thus allowing irradiation of a variety of physical shapes.
- The electron beam radiation process is practically free of waste products, and therefore is no serious environmental hazard.

### 2.2.2 Gamma Rays

Gamma rays (or γ-rays) represent electromagnetic radiation emitted from excited atomic nuclei of unstable atoms (radionuclides) as an integral part of the process whereby the nucleus rearranges itself into a state of lower excitation (that is, lower energy content). A gamma ray is a packet of electromagnetic energy—a photon. These photons are the most energetic ones in the electromagnetic spectrum. Essentially, they are emitted by *radioactive decay* and have energies in the range from $10^4$ to $10^7$ eV. All γ-rays emitted from a given *radioactive isotope* have the same energy. Gamma rays penetrate matter tissues farther than *beta* or *alpha* particles, producing ionization (electron disruption) in their path. In living cells these disruptions result in damage to the DNA and other cellular structures, eventually causing the death of the organism or rendering it incapable to reproduce. The gamma radiation does not create residuals or impart radioactivity in the materials exposed to it. They are similar to x-rays (see below).

The most widely used radioactive isotopes in medical and industrial applications are cobalt 60 ($^{60}C$), cesium 137 ($^{137}Cs$), and iridium 192 ($^{192}Ir$). The half-life of $^{60}C$ is 5.3 years, that of $^{137}Cs$ is 30 years, and the half-life of $^{192}Ir$ is 74 days.[22] When used for irradiation the isotope is generally in the form of a pellet size, $1.5 \times 1.5$ mm, loaded into a stainless steel capsule and sealed. Unlike electron beam or x-rays, gamma rays cannot be turned off.

Once radioactive decay starts, it continues until all the atoms have reached a stable state. The radioisotope can only be shielded to prevent exposure to the radiation. The most common applications of gamma rays are sterilization of single-use medical supplies, elimination of organisms from pharmaceuticals, microbial reduction in and on consumer products, cancer treatment, and processing of polymers (cross-linking, polymerization, degradation etc.).

### 2.2.3 X-Rays

X-radiation (also called Röntgen radiation) is a form of electromagnetic radiation. X-rays have a wavelength in the range from 10 to 0.01 nm, corresponding to frequencies ranging from $3 \times 10^{16}$ to $3 \times 10^{19}$ and energies in the range of 120 eV to 120 keV. They are shorter in wavelength than UV rays. Their name comes from their discoverer, Wilhelm Conrad Röntgen, who called them x-rays to signify an unknown type of radiation.[23]

X-rays span three decades in wavelength, frequency, and energy. From about 0.12 to 12 keV they are classified as soft x-rays, and from 12 to 120 keV as hard x-rays, due to their penetrating abilities. X-rays are a form of ionizing radiation, and as such, they can be dangerous to living organisms.

There are two different atomic processes that can produce x-ray photons. One process produces *bremsstrahlung* radiation (see Section 2.2.1) and the other produces K-shell or characteristic emission. Both processes involve a change in the energy state of electrons. X-rays are generated when an electron is accelerated and then made to rapidly decelerate, usually due to interaction with other atomic particles. In an x-ray system, a large amount of electric current is passed through a tungsten filament, which heats the filament to several thousand degrees centigrade to create a source of free electrons. A large potential is established between the filament (the cathode) and a target (the anode). The two electrodes are in a vacuum. The electrical potential between the cathode and anode pulls electrons from the cathode and accelerates them as they are attracted toward the anode, which is usually made of tungsten. X-rays are generated when free electrons give up energy as they interact with the orbital electrons or nucleus of an atom. The interaction of the electrons in the target results in the emission of a continuous *bremsstrahlung* spectrum and also characteristic x-rays from the target material. Thus, the difference between γ-rays and x-rays is that the γ-rays originate in the nucleus and x-rays originate in the electrons outside the nucleus (surrounding it) or are produced in an x-ray generator.[24–27]

X-rays are primarily used for diagnostic radiography in medicine,[28] and in crystallography. Other notable uses are x-ray microscopic analysis, x-ray fluorescence as an analytical method, and industrial radiography for inspection of industrial parts, such as tires and welds.

There are reports and patents covering the use of x-rays in processing of a variety of parts made from polymers, particularly in the form of advanced fiber-reinforced composites.[29–33]

### 2.2.4 Other Types of Ionizing Radiation

Subatomic particles other than electrons, such as positrons and protons, can be accelerated to high velocities and energies, usually expressed in terms of center-of-mass energy, by machines that impart energy to the particles in small stages or nudges, ultimately achieving very high-energy particle beams, measured in terms of billions and even trillions of electron volts. Thus, in terms of their scale, particles can be made to perform as powerful missiles for bombarding other particles in a target substance or for colliding with each other as they assume intersecting orbits.

High-energy beams involving the above particles are created in particle accelerators, in which a charged particle is drawn forward by an electro-static field with a charge opposite that of the particle (like charges repel one another, opposites attract); as the particle passes the source of each field, the charge of the field is reversed so that the particle is now pushed onto another field source.

An *ion beam* is a type of particle beam consisting of ions. High-energy ion beams are produced like electron beams by particle accelerators, with the difference that a *cyclotron*, another particle accelerator, is used (see Figure 2.4). Cyclotrons accelerate charged particles using a high-frequency, alternating voltage (potential difference). A perpendicular magnetic field causes the particles to spiral almost in a circle so that they reencounter
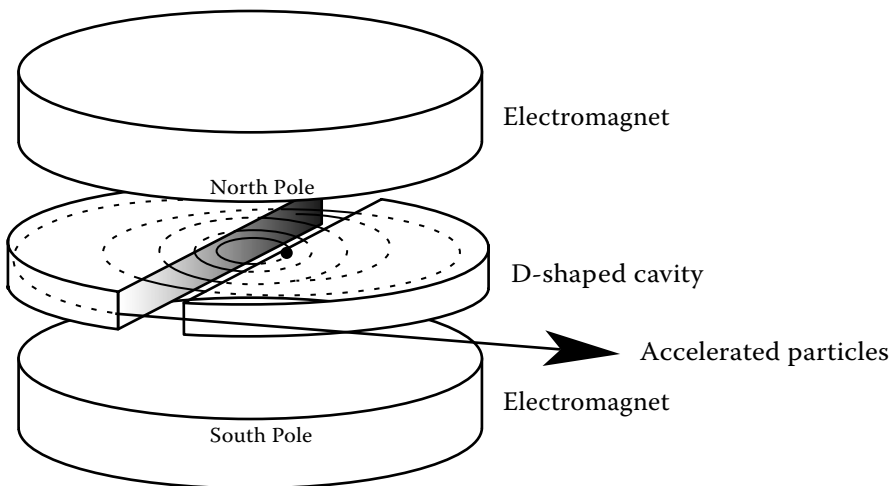


**FIGURE 2.4**
Schematic of a cyclotron.

the accelerating voltage many times. Irradiation effects of an ionic beam are different from the ionizing radiation (gamma rays and EB) due to differences in *linear energy transfer* (LET), the average energy deposited in the material used by a projectile particle along its path. In general, the LET of an ion beam is larger than that of gamma rays and electron beam, depending on the particle mass and energy. Applications of ionic beams reported in literature are in modifications of mechanical properties of carbon-fiber-reinforced plastics,[34,35] surface modification of polytetrafluoroethylene,[36] and the production of fuel cells.[37]

## 2.3  Comparison of UV and EB Processes

In summary, the initiation of polymerization and cross-linking reactions in polymeric systems is different for these two processes. Most of the events initiated by UV radiation, i.e., by photons, occur near the surface, because the photon absorption is governed by the Beer-Lambert law (see Section 4.1). In contrast, the reactive species produced by electron beam are dispersed randomly throughout the entire thickness of the material (see Figure 2.5). The penetration depths as well as the amount of energy (i.e., dose) deposited can be regulated with a great deal of accuracy (see Section 5.1). In spite of these differences, the two processes can be used for the same or similar applications, such as printing, coatings, and adhesives, that is, where only thin layers are being processed. However, for thicker layers, films, and sheets, even opaque and highly filled, as well as composite materials, electron beam radiation is the method of choice. Other issues regarding the differences between UV and EB processes and applications are in Chapter 1. The recent developments of EB equipment, which represent substantial size and power reductions, enable the EB process to become an alternative to the UV process in several applications, such as graphic arts, where previously only UV equipment was used.



Ultraviolet Light                         Electron Beam
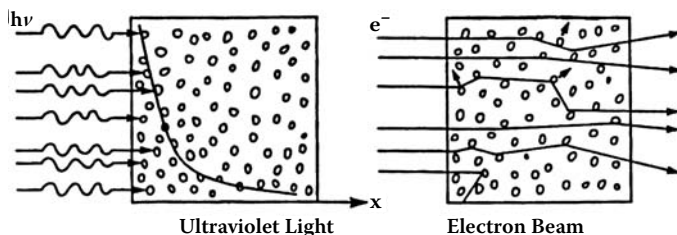
**FIGURE 2.5**
Comparison of UV and EB radiations ($r_0$ = substrate thickness).

The other types of ionizing radiation mentioned above are also used in processing of polymeric systems, but not as frequently as electron beams and mainly for specialized applications.

## References

1. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R. W., and Berejka, A., *UV&EB Curing Technology and Equipment*, Vol. I, John Wiley and Sons, Chichester/SITA Technology, London, p. 49 (1998).
2. Kosar, J., *Light Sensitive Systems*, John Wiley & Sons, New York (1966).
3. Koleske, J. V., *Radiation Curing of Coatings*, ASTM International, West Conshohocken, PA, p. 30 (2002).
4. *American Institute of Physics Handbook* (Gray, D. E., Ed.), McGraw-Hill, New York (1983).
5. Yasuda, H., *Plasma Polymerization*, Academic Press, Orlando, FL (1985).
6. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R. W., and Berejka, A., *UV&EB Curing Technology and Equipment*, Vol. I, John Wiley & Sons, Chichester/SITA Technology, London, p. 45 (1998).
7. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R. W., and Berejka, A., *UV&EB Curing Technology and Equipment*, Vol. I, John Wiley & Sons, Chichester/SITA Technology, London, p. 12 (1998).
8. Frank, J. D., Cekic, M., and Wood, H. C., *Proceedings of the 32nd Microwave Power Symposium*, Ottawa, Canada, p. 60 (1997).
9. Eliasson, B., Kogelschatz, U., *Appl. Phys.*, B46, p. 299 (1988).
10. Davidson, R. S., *Exploring the Science, Technology and Applications of U.V. and E.B. Curing*, SITA Technology, London, p. 14 (1999).
11. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R. W., and Berejka, A., *UV&EB Curing Technology and Equipment*, Vol. I, John Wiley & Sons, Chichester/SITA Technology, London, p. 49 (1998).
12. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R. W., and Berejka, A., *UV&EB Curing Technology and Equipment*, Vol. I, John Wiley & Sons, Chichester/SITA Technology, London, p. 83 (1998).
13. Roth, A., *RadTech Europe '97, Conference Proceedings* (June 16–19, Lyon, France), p. 92 (1997).
14. Rhodes, Ch. K., *Excimer Lasers, Topics Applied Physics*, Vol. 30, Springer, Berlin (1984).
15. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R. W., and Berejka, A., *UV&EB Curing Technology and Equipment*, Vol. I, John Wiley & Sons, Chichester/SITA Technology, London, p. 93 (1998).
16. Eckstrom, D. J. et al., *J. Appl. Phys.*, 64, p. 1691 (1988).
17. Samuel, A. H., and Magee, J. L., *J. Chem. Phys.*, 21, p. 1080 (1953).
18. *Irradiation Effects on Polymers* (Clegg, D. W., and Collyer, A. A., Eds.), Elsevier, London (1991).
19. *Radiation Processing of Polymers* (Singh, A., and Sliverman, J., Eds.), Carl Hanser Verlag, Munich (1992).

20. Mehnert, R., in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A22 (Elvers, B., Hawkins, S., Russey, W., and Schulz, G., Eds.), VCH, Weinheim, p. 471 (1993).
21. Garratt, P. G., *Strahlenhärtung*, Curt R. Vincentz Verlag, Hannover, p. 61 (1996). In German.
22. NDT Resource Center, www.ndt-ed.org (June 7, 2009).
23. Kevles, B. H., *Naked to the Bone Medical Imaging in the Twentieth Century*, Rutgers University Press, Camden, NJ, p. 19 (1996).
24. Dendy, P. P., and Heaton, B., *Physics for Diagnostic Radiology*, CRC Press, Boca Raton, FL, p. 12 (1999).
25. Feynman, R., Leighton, R., and Sands, M., *Feynman Lectures on Physics*, Vol. 1, Addison-Wesley, Reading, MA, p. 2 (1963).
26. L'Annunziata, M., and Baradei, M., *Handbook of Radioactivity Analysis*, Academic Press, New York, p. 58 (2003).
27. Grupen, C., Cowan, G., Eidelman, S. D., and Stroh, T., *Astroparticle Physics*, Springer, Berlin, p. 109 (2005).
28. Smith, M. A., Lundahl, B., and Strain, P., *Medical Device Technology*, 16, No. 3, April, p. 16 (2003).
29. Ramos, M. A., Catalao, M. M., Schacht, E., Mondalaers, W., and Gil, M. H., *Macromolecular Chemistry & Physics*, 203, No. 10–11, July 29, p. 1370 (2002).
30. Wang, C.-H., et al., *J. Phys. D*, 41, p. 8 (2008).
31. Sanders, C. B., et al., *Radiat. Phys. Chem.*, 46, p. 991 (1995).
32. Berejka, A. J., *RadTech Report*, 16, No. 2, March/April, p. 33 (2002).
33. Galloway, R. A., Berejka, A. J., Gregoire, O., Clelland, M. R., U.S. Patent Application 20080196829, August 21 (2008).
34. Kudoh, H., Sasuga, T., and Seguchi, *Radiat. Phys. Chem.*, 48, p. 545 (1996).
35. Seguchi, T., et al., *Nucl. Instrum. Meth. Phys. Res. B*, 151, p. 154 (1999).
36. Choi, Y. J., Kim, M. S., and Noh, I., *Surface Coatings Technol.*, 201, p. 5724 (2007).
37. Yamaki, T., et al., in *Proceedings of Conference Proton Exchange Fuel Cells* (October 29–November 3, Cancun, Mexico) (2006).

# 3

## UV and EB Curing Equipment

### 3.1 UV Curing Equipment

There are well over 100,000 high-intensity ultraviolet curing units in industrial use. Their main applications are surface curing of inks, coatings, and adhesives. They typically operate in the 200450 nm wavelength range, with lamp power as high as 240 W/cm (600 W/in.) of lamp length.[1]

The UV curing equipment consists essentially of the following three components:

1. *Lamp (or bulb)*. The electrical energy supplied to the bulb is converted into UV energy inside the bulb.
2. *Lamp housing*. The housing is designed to direct and deliver to the substrate or the part to be irradiated. The lamp housing contains the reflector that focuses the ultraviolet energy generated by the lamp. Also referred to as the irradiator.
3. *Power supply.* The power supply delivers the energy needed to operate the UV lamp.

A typical UV curing unit may house one or more lamps. Most frequently, the material to be cured is passed underneath one or more lamps using a moving belt. The speed of the belt determines how long the web is exposed to the UV. The UV generated by the lamp is reflected by a reflector, which may either focus or defocus it, depending on the process.

The lamp performance, which affects cure, is expressed by the following characteristics:[2]

1. *UV Irradiance* is the radiant power arriving at a surface per unit area. The most commonly used unit of irradiance is W/cm$^2$. It varies with lamp output power, efficiency, the focus of its reflector system, and its distance to the surface. The intense peak of focused power directly under the lamp is referred to as *peak irradiance.* Although not a defined term, *intensity* is occasionally used to refer to irradiance. Irradiance

incorporates all of the contributing factors of electrical power, efficiency, radiant output, reflectance, focus, bulb size, and lamp geometry. Higher irradiance at the surface will produce correspondingly higher light energy within the coating. The depth of cure is affected more by irradiance than by the length of exposure. The effects of irradiance are more important for higher absorbance (more opaque) films. Higher irradiance can permit the use of less photoinitiator.[2]

2. *UV exposure* is the radiant energy per unit area arriving at a surface. UV exposure represents the total quantity of photons arriving at a surface in contrast to irradiance, which is the rate of arrival. Exposure is inversely proportional to speed under any given light source, and proportional to the number of exposures (in multiple rows of lamps it is the number of "passes"), and is the time integral of irradiance with the usual units $J/cm^2$ and $mJ/cm^2$. It is simply the accumulated energy to which the surface was exposed.

3. *Infrared radiance* is the amount of infrared energy primarily emitted by the quartz envelope of the UV source. This energy is collected and focused with the UV energy on the surface of the substrate to the extent depending on the IR reflectivity and efficiency of the reflector. Infrared radiation can be expressed in exposure or irradiance units, but most commonly, the surface temperature it generates is of primary interest. The heat it produces may be a benefit or a nuisance.[2]

4. *Spectral distribution* describes the relative radiant energy as a function of the wavelength emitted by a bulb or the wavelength distribution of energy arriving at a surface and is often expressed in relative (normalized) terms. It can be displayed as a plot or a table, and in this form it allows comparison of various bulbs and can be applied to calculations of spectral power and energy.[2]

### 3.1.1 Lamps

There are a large number of lamps used to initiate the reactions in the processed material. They differ in design and source of radiation. Below is a list of commercially available lamps:[3]

- Mercury lamps (low, medium, and high pressure)
- Electrodeless (microwave-powered) lamps
- Excimer lamps
- Xenon lamps (free running and pulsed)
- Spot cure lamps
- Continuous wave (CW) and pulse lasers
- Light-emitting diodes
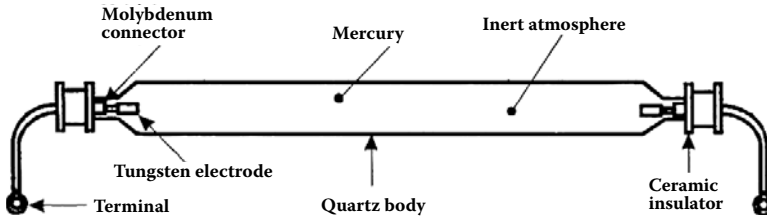
**FIGURE 3.1**
Medium-pressure mercury lamp. (Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, SITA Technology Ltd., London, p. 72 (1998). With permission from SITA Technology Ltd.)

While any of the above sources find specific applications, medium-pressure mercury (microwave and arc) and xenon lamps are most widely used in industrial applications.

### 3.1.1.1 Medium-Pressure Lamps

The most frequently used lamp for UV curing processes is medium-pressure mercury lamp. Its emission spectrum can be used to excite the commonly used photoinitiators. Moreover, this type of lamp has a relatively simple design, is inexpensive, can be easily retrofitted to a production line, and is available in lengths up to 8 ft (2.5 m). Power levels in common use are in the range 40 to 240 W/cm, and even higher levels are available for special applications.[3]

A medium-pressure mercury arc lamp consists of a sealed cylindrical quartz tube with tungsten electrodes on each end. The tube contains a small amount of mercury and starter gas (usually argon). An example of such a lamp is in Figure 3.1.[4]

The spectral output of the medium-pressure lamp can be altered by "doping," i.e., adding a small amount of metal halide to the fill material, with mercury. Commonly doped lamps are iron and gallium lamps.[5] Medium-pressure lamps have long lifetimes (typically in excess of 3,000 h), although the intensity of the emitted light and the relative intensity of the spectral lines change with time. This affects their performance to the point that
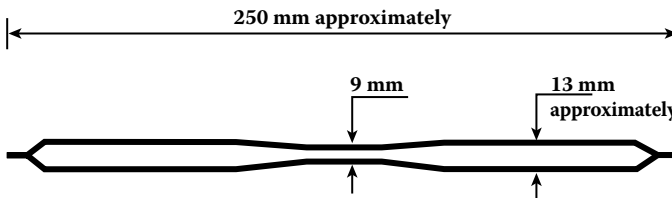


**FIGURE 3.2**
Electrodeless lamp. (Courtesy of Hanovia.)

the lamp might strike but the output is so low that it does not trigger the reaction. Therefore, it is necessary to check its output periodically by a spectroradiometer.

### 3.1.1.2  Electrodeless Lamps

Electrodeless lamps have emission spectra similar to those of medium-pressure doped and undoped lamps (the manufacturers often use the term *additive lamps*). They are actually medium-pressure mercury lamps, but they differ from arc lamps in that the tubes do not have electrodes (see Figure 3.2). The excitation of mercury atoms is by microwave power generated by magnetrons. The system containing the power modules (magnetrons) and reflectors is integral, and because of that, it is somewhat larger than the equivalent medium-pressure arc lamp system. This has to be taken into consideration when designing or retrofitting a line. The currently available width of the lamp is up to 26 cm (10 in.). The modules are designed so that when wider webs are processed, several modules are mounted end to end to cover any width, with virtually no interruption to the continuous line of focused UV across the web.

In the current design of an electrodeless microwave-powered lamp, the microwave energy is generated by two 1.5 or 3.0 kW magnetrons with a frequency of 2,450 MHz and fed through an antenna system to each waveguide. The microwave energy coupled with precisely designed slots is uniformly distributed over the length of the bulb. Magnetrons and waveguides are cooled by filtered air, which is also passed into the microwave chamber through small holes in the reflector. This downward airflow cools the lamp and keeps the lamp and the reflector clean.

In general, the electrodeless lamp contains a small amount of mercury and a neutral starter gas. The mercury pressures during its operation are in the 5–20 bar range, which is higher than for arc lamps, with pressures only in the 1–2 bar range. The characteristics of the lamp can be modified by the addition of metal halides in controlled quantities to the gas. The frequently used D or V lamps contain iron or gallium salts, respectively.[6] Some characteristics of microwave-powered lamps are in Table 3.1.

A variety of gas fills are available, and these cover a fairly large range of UV and visible spectra. The bulbs are interchangeable and can be changed easily, so it is easy to use the proper lamp for a specific job. The advantages of the electrodeless lamp systems are:

- The modular lamp-reflector system is simple and easy to install and change.
- The bulb does not decrease in output or in its spectral distribution during its entire life.
- They have longer lifetimes than arc lamps (4,000 to 6,000 h vs. 1,000 to 1,500 h).

**TABLE 3.1**

Characteristics of Electrodeless Lamps

| Lamp System | Bulb Type | Bulb Diameter, mm | Peak Irradiance, W/cm² (UVA) |
|---|---|---|---|
| F-450 (350W/in.) | H | 9 | 2.5 |
| | D | 9 | 6.0 |
| | V | 9 | 2.0 |
| F-450 (350W/in.) | D | 13 | 5.1 |
| | D | 11 | 5.6 |
| | D | 9 | 6.0 |
| F-600 (560 W/in.) | H | 13 | 2.7 |
| | D | 13 | 8.0 |
| | V | 13 | 2.4 |
| F-600 (560 W/in.) | D | 13 | 8.0 |
| | D | 11 | 9.6 |
| | D | 9 | 9.9 |

*Source:* Courtesy Fusion UV Systems.

- They have short warm-up times (2 to 3 s).
- After being switched off, the lamps do not have to cool down before reigniting.

Disadvantages of electrodeless lamps are mainly associated with the cost of the equipment maintenance, since the magnetrons have to be replaced every about 5,000 to 8,000 h. Additional shortcomings are higher cost of power due to lower efficiency of the microwave generating process. In a multiple-lamp system, multiple bulbs and magnetrons are replaced, and the cost is a trade-off of the longer operating life and stability of exposure.

### 3.1.1.3 Low-Pressure Mercury Lamps

Low-pressure mercury lamps consist most frequently of a quartz cylinder with electrodes on both ends, although other shapes are also produced.[7] Inside the lamp is a mixture of mercury and argon at a pressure of $10^{-2}$ to $10^{-3}$ Torr. The emission from this lamp is 254 nm, and with high-quality quartz, some light with 189 nm wavelength is produced. Low-pressure lamps are of low power, and therefore are not used for the cure of coatings, but are well suitable for applications where slow cure rate is tolerated, such as liquid crystal displays or in resist technology for the production of microchips.

### 3.1.1.4 High-Pressure Mercury Lamps

High-pressure mercury lamps operate at pressures of about 10 atm, and there are essentially two types used in industrial applications. The *point source*

*lamp* focuses on a small-diameter spot, thus delivering an intense radiation to that spot. The *capillary lamp* is used for narrow webs up to approximately 20 cm (8 in.) wide.[4] They are capable of producing a wider and more continuous spectrum than the medium-pressure lamps and operate with higher power (150–2,880 W/cm). Their disadvantage is a relatively short operating life, typically hundreds of hours.

### 3.1.1.5 Excimer Lamps

Excimer lamps are quasi-monochromatic light sources available in UV wavelengths. The light is produced by silent electrical discharge through gas in the gap between two concentric quartz tubes. Electronically activated molecules are produced in the gas phase and decompose within nanoseconds to produce photons of high selectivity. This process is similar to the process in excimer lasers.

The most important difference between excimer and standard UV lamps is that the former are incoherent radiation sources and can therefore be used for large area applications. Different wavelengths can be produced by choosing different gas fills in the gap between the quartz tubes.

The wavelength of the emitted light depends on the choice of atoms. Besides the principle of excimer formation, the technical parameters for the lamp and discharge are responsible for the quasi-monochromatic character of the emitted spectrum. The most important commercial excimers are formed by electronic excitation of molecules of rare gases ($He_2$, $Ne_2$, $Ar_2$, $Kr_2$, and $Xe_2$), rare-gas halides (e.g., ArF, KrF, XeCl, and XeF), halogens, and mercury halogen mixtures (HgCl, HgBr, and HgI). They are unstable and decay by spontaneous optical emission. The lamp is completely free of ozone.[8] Currently, excimer lamps with wavelengths of 308, 222, and 172 nm are commercially available.

Stimulated (laser) excimer emission can be generated in pulsed high-pressure glow discharges. Dielectric barrier (silent) discharges[9] or microwave discharges[10] can be used to produce quasi-stationary or continuous incoherent excimer radiation.

With the narrow range of wavelength of the excimer lamp, a specific initiator can be selected with the maximum efficiency in that range. Thus, it is possible to reduce the amount of photoinitiator from that used for conventional UV sources and reduce the cost of the material and amounts of unreacted initiator in the finished coated substrate.[11] Excimer lamps can be used for both free radical and cationic photoinitiators.[12]

Currently, there are two types of commercial excimer lamps: barrier-discharge- and microwave-driven lamps.

### 3.1.1.5.1 Barrier-Discharge-Driven Excimer Lamps

The excimer lamp of this type is made by Heraeus Noblelight (Hanau, Germany) and consists of two concentric cylindrical quartz tubes, fused together on both ends. The excimer gas mixture is filled in the gap between the two tubes and sealed. The electrodes are placed outside the discharge
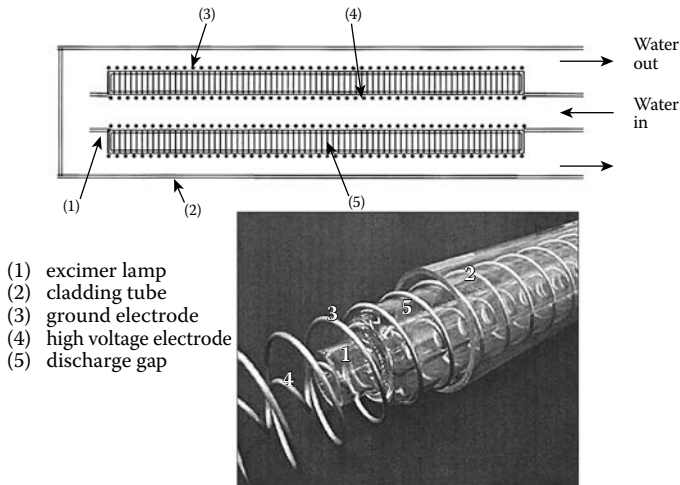
**FIGURE 3.3**
Barrier discharge excimer lamp. (Courtesy of Heraeus Noblelight.)

gap (Figure 3.3). They transfer a high-frequency alternating voltage through a barrier discharge into the gas, where the excimers are formed. This technology allows the lamps to work in both continuous and pulsating modes.

IR radiation is not produced, and therefore the lamps are relatively cold, with the surface temperatures being in the range 35–40°C (95–104°F).[12] This makes them suitable for heat-sensitive substrates.

In addition to the low surface temperature, excimer lamps have the advantage that they start immediately, so they can be switched on and off as needed. There is no need for standby function and for a shutter system, so no movable parts are necessary on the radiation head. Both continuous and pulse mode operation is possible. The lamps are very compact, which is particularly important for the printing industry, because it is possible to retrofit them into the existing process.

The excimer curing system of this design consists of the following components:[8]

- Bulb of different radiation length in an optimized compact housing
- Power supply
- Cooling unit (using deionized water)
- Inertization (optional)

These lamps are radio frequency (RF) powered, and can be easily controlled and switched. The power supply includes all electrical controls, interlocks, and the water cooling supply system.[13] A complete system is shown schematically in Figure 3.4.
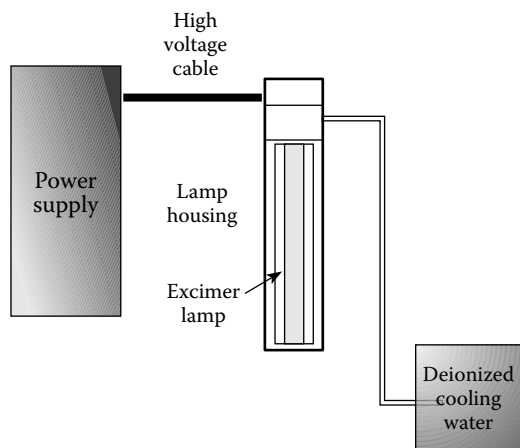
**FIGURE 3.4**
UV curing system with a barrier discharge excimer lamp. (Courtesy of Heraeus Noblelight.)

The nature of this design of excimer UV lamps makes them particularly effective in flexo and offset printing. The advantages cited in these applications[8] are:

- No heating of the substrate or press
- Improved print quality, since there is no pixel displacement due to film distortion
- Reduced smell of inks (the lamp operates in a nitrogen atmosphere) and substrates (due to low operating temperature)
- Reduced press downtime since the lamp does not need warm-up after being switched on or reignited
- Compact excimer curing system that can therefore be easily retrofitted into existing equipment

One interesting application of barrier charge excimer lamps is surface matting of acrylate coatings with a wavelength of 172 nm and subsequent UV or electron beam (EB) cure of the entire thickness of the film. The advantage is that no matting additives are needed and the line speeds are much higher than those in the traditional process[8] (see Section 7.1.5).

Due to relatively low UV radiant power of these types of lamps, nitrogen inerting has to be used,[14] which increases the operating cost.

### 3.1.1.5.2 Microwave-Driven Excimer Lamps

Fusion Systems (Gaithersburg, MD) at one time offered 240 W/cm microwave-driven excimer lamps within its VIP (Versatile Irradiance Platform) series. They were among the most powerful sources of UV radiant power,[15] available

in XeCl (peak wavelength 308 nm) and CuBr (peak wavelength 535 nm). These lamps are no longer commercially available.

### 3.1.1.6 Xenon Lamps

Xenon lamps are available mainly as tubular and point source bulbs. The radiation produced by this type of lamps is not particularly rich at wavelengths below 400 nm, and therefore their applications are somewhat limited. However, it is possible to pulse xenon lamps, which enables them to achieve high peak irradiances. Commercially available pulsed xenon lamps are available with emissions in the UV and visible spectral range. Alternating the gas fill can produce output rich in UV.

The advantages of pulsing xenon lamps are:

- The pulses are short; consequently, there is no significant heat buildup.
- There is no need to increase temperature to evaporate mercury; thus, xenon lamps operate at considerably lower temperatures.
- The lamps can be turned off completely in microseconds, and thus there is no continuous infrared radiation and no shutters have to be installed.
- There is no need for nitrogen inerting.
- With its high peak power, pulsed light penetrates opaque materials more effectively than does continuous light.

Because of the cooling period between pulses, these lamps operate at much lower temperatures and are suitable for manufacturing processes where the product does not tolerate high temperatures.

Xenon lamps do not generate ozone, and thus can be used in processes where the materials are sensitive to ozone. An additional advantage is that there is no need for plant ventilation systems for the removal of ozone.

Pulsed curing systems are widely used in the manufacture of medical devices, electronics, semiconductors, and optical fibers. Pulsed xenon lamps can be made in a variety of shapes to fit specific requirements, such as 360° illumination. Examples of different designs are in Figures 3.5 and 3.6.

### 3.1.2 Lamp Housing

The lamp housing has the function to direct and deliver the energy to the substrate or piece being cured. The reflector system contained in the housing reflects the energy generated by the lamp and the way it depends on its design. The older, parabolic reflectors just reflected the energy in flood pattern. Semielliptical reflectors direct the energy to a focal point. The newest type, elliptical reflectors with a greater wrap around the lamp, delivers a more focused energy distribution forming a narrow curing zone with an
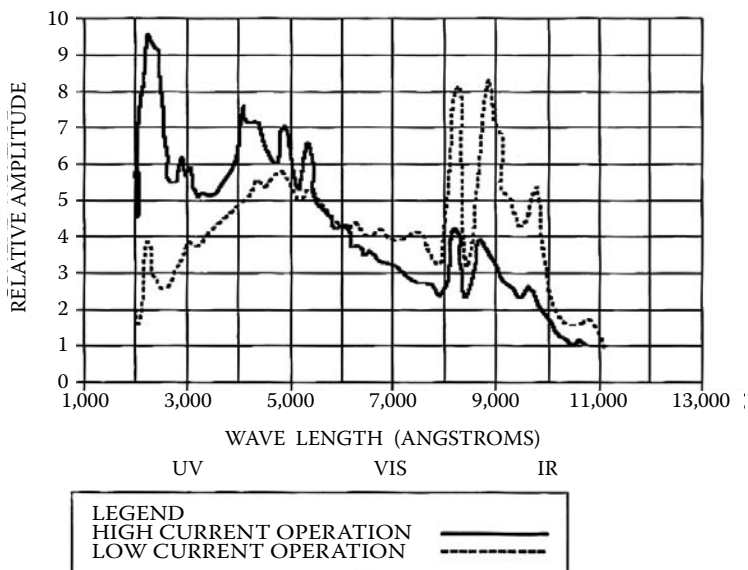
**FIGURE 3.5**
Spectral dependence of a xenon lamp on electrical operating parameters. (Courtesy of Xenon Corporation.)
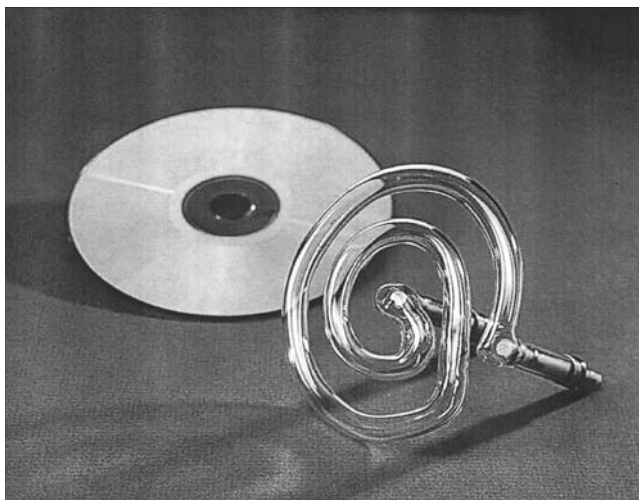


**FIGURE 3.6**
Spiral xenon lamp used for DVD bonding. (Courtesy of Xenon Corporation.)

**PARABOLIC**
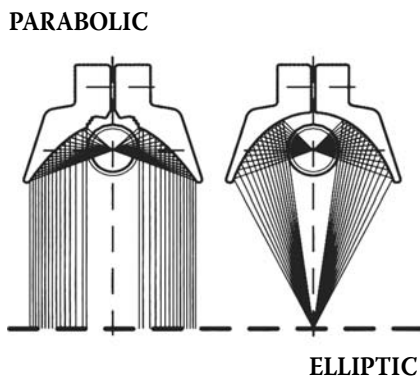


**ELLIPTIC**

**FIGURE 3.7**
Two basic designs of reflectors. (Courtesy of IST America.)

increased amount of energy at the far focal point. With the development of 3D processes and the many surfaces of a piece that need to be exposed to UV, semielliptical reflectors will likely be used more frequently. It is quite possible that new reflector designs will soon appear.[16] The two basic reflector designs are depicted in Figure 3.7.

The material that will reflect the entire range of UV wavelengths is *pure* aluminum. UV reflectors are made from highly polished (specular) sheet (mill) aluminum with vapor-deposited aluminum on the surface with a protective inorganic overcoat. Reflector supports, which provide the proper curvature of the reflector, are made from extruded aluminum or castings in different lengths and shapes, and they are also designed to provide lamp cooling. Arc lamp electrode seals must be kept below 250°C (482°F), the lamp jacket must be kept under 600 to 800°C (1,110 to 1,470°F), and aluminum starts to deteriorate above 250°C (482°F). Air cooling or water cooling systems are used to help cool the lamp seals and quartz jacket.[17] By contrast, microwave-powered bulbs are maintained at a nearly constant temperature over their entire length, reducing stress on the quartz, and simultaneously reducing the generation of ozone.

Only a perfectly smooth surface exhibits directed (specular) reflection, i.e., where the angle of reflectance equals the angle of incidence. This, however, is not the case under real-life conditions, where the surface micro-roughness cannot be avoided, and consequently, the UV can be slightly diffused over a finite range of reflection angles.[17]

UV reflectors also reflect radiation energy in the visible and infrared (IR) energy spectral regions at least as efficiently as in the UV region.[16,17] This is undesirable in such cases where the substrate or the piece being irradiated is heat sensitive. To overcome this, the surface of the reflector is coated with
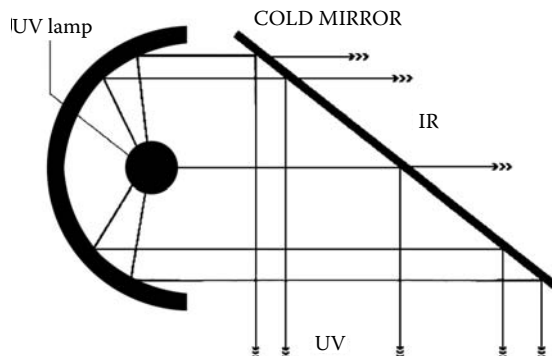
**FIGURE 3.8**
Example of a cold mirror reflector. (Courtesy of Honle UV America.)

special dielectric coatings ("cold mirror"), which, when applied in multiple layers, will reflect UV but transmit visible and IR energy. An example of a cold mirror reflector is in Figure 3.8.

Often, in order to contain an inert atmosphere in the curing zone, a quartz plate or window is placed between the lamp and the substrate. The filter must be cooled sufficiently to prevent it from becoming an IR re-radiation source itself.[16] The disadvantage of this design is that part of the UV transmission is lost, and the plate also interferes with the air cooling of the substrate. A few designs use water-cooled reflectors, but this only cools the lamp and does not alter the IR or visible energy reflected to the substrate. In some designs, two quartz cooling tubes are placed between the lamp and the substrate. Deionized water circulates through the tubes. Up to 50% of the infrared emission from the lamp can be absorbed by this type of filter,[18] although there is also a significant reduction in the UV. An additional control of IR energy is to coat the filter with a reflective coating ("hot mirror"), which reflects a limited amount of the IR radiation back to the reflectors without significantly affecting the transmitted UV.[16,18] For this to function properly, the reflector in the lamp housing must absorb the reflected IR.

In practical applications, some lamps, notably medium-pressure mercury arc lamps, cannot be started or restarted instantaneously and need some time for restrike. Interruption of lamp action would be totally unacceptable in continuous production. Moreover, the heat from burning lamps could cause deterioration of the substrate if the line is in standby mode (stopped). Therefore, shutters (see Figure 3.9) are installed that close over the lamp, which is immediately switched to half power. Shutters can be incorporated in the reflector design, in a clamshell fashion, or may rotate to enclose the lamp.[19] Shutters are not normally used with microwave-powered lamps, as they are virtually instant on and off.
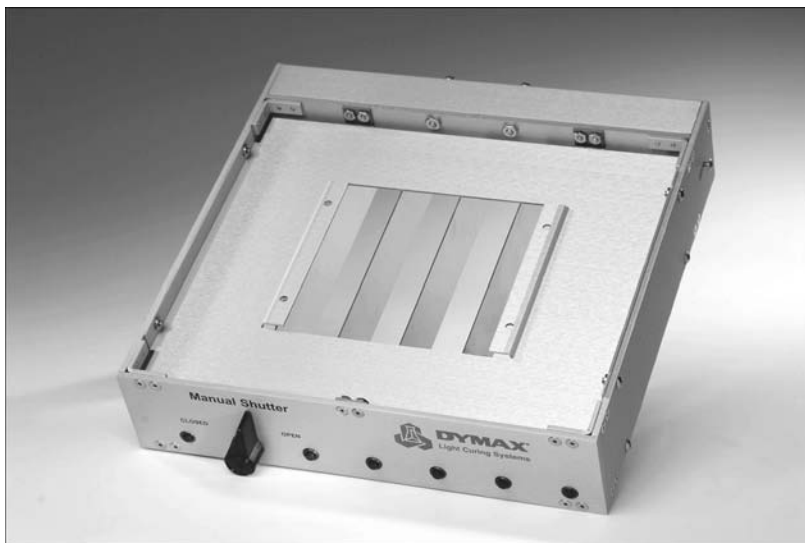
**FIGURE 3.9**
Manual shutter open. (Courtesy of Dymax Light Curing Systems.)

### 3.1.3  Power Supply and Controls

#### 3.1.3.1  Power Supply Systems

Until recently, a typical power supply would only operate at discreet power levels, some going from standby to high, others supplying medium power. This is sufficient for most curing processes, but limits the capability of the user to control a highly specialized process.

This type of power supply often limits the process speed, which in turn means that the energy usage could be much more than required for the given chemical curing system. When operating at high power, the by-products of generating UV energy, such as heat and visible light, are at their most intense.[16]

Medium-pressure mercury arc lamps are normally powered by AC. Because of the high impedance of the plasma arc in the lamp, the maintenance of plasma requires a high electrode potential. The required potential gradients are up to 30 V per centimeter of length, and the open-circuit voltage should be up to twice the operating voltage. This means that main voltage is insufficient for practically all lamps. Therefore, in order to ignite and operate the lamp, a step-up transformer is required. Other important factors entering the design of the power supply are:[20]

- To ignite and operate the lamp, a step-up transformer is required.
- Due to negative voltage-current characteristics of the lamp discharge, a current limiting power supply must be used.
- The burn-in characteristics of the arc lamps have to be taken into account.
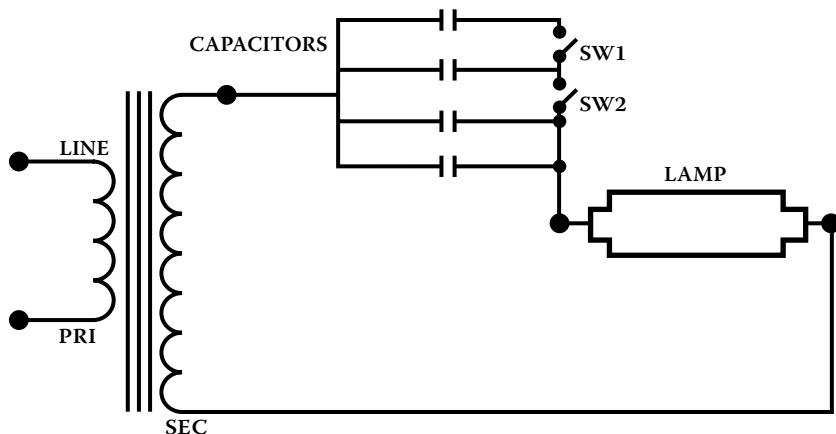
**FIGURE 3.10**
Power supply for mercury lamps.

Immediately after ignition, mercury is still liquid and the discharge takes place in the fill gas (argon). At this point the voltage is low and the current is limited essentially by the short-circuit current delivered by the power supply. As the temperature within the lamp increases, mercury vaporizes. The lamp impedance increases, and this causes the lamp voltage to increase and the current to decrease. After about 1 min, the burn-in period is finished and the lamp reaches stationary conditions.

The most common type of power supplies for mercury lamps with large arc lengths combine a step-up transformer and a "ballast" capacitor placed in the secondary circuit of the transformer (see Figure 3.10). Since the lamp power depends on its capacitance, the step-wise power can be simply varied by switching capacitors as long as the lamp is operated at appropriate cooling conditions.

Electrodeless medium-pressure mercury lamps are powered by microwave energy. The system contains either one or two microwave generators, two waveguides, and a closed nonresonant microwave chamber formed by a semielliptic metallic reflector with flat ends and a fine metal mesh.[21] Microwave energy is generated by one or two 1.5 to 3.0 kW, 2,450 MHz magnetrons and fed through an antenna system to each waveguide. The metallic reflector and the metal screen closure mesh form a microwave chamber, which, from the electrical point of view, has a noncavity structure. The microwave energy coupled into the chamber by precisely designed slots is uniformly distributed over the lamp tube. Standing waves, which would result in resonant distribution of microwave energy, are avoided by slot design and choosing pairs of magnetrons slightly differing in frequency in lamps using two magnetrons. Magnetrons and waveguides are cooled by filtered

air, which is also passed into the microwave chamber through small holes in the reflector. This downward airflow also cools the bulb and keeps the bulb and reflector clean.[22] The power supply also contains a filament heating transformers, a control board with status, and fault indicators and numerous safety and production interlocks.

### 3.1.3.2 Control Systems

Currently, there are several control systems for UV power supplies. One design is based on the use of a transductor as inductive ballast and current control at the same time. The current flowing through the lamp is controlled by premagnetization of the transductor. This allows a continuous lamp power control within 40 to 100%. Besides the continuous current control, smooth lamp burn-in, a short dark period between the AC half-waves, early reignition after each voltage half cycle, and other benefits result.[23] Another means of achieving stepless control of current in the lamp is by using thyristors. When compared to transductor control, the dark period is not constant, but increases at lower levels of power.[23]

In general, with the above controls, the lamp power depends on the fluctuations of the main voltage. This may cause fluctuations in irradiance and potentially reduce the quality of the product. This can be avoided by using a closed-loop control circuit.[24]

In a closed-loop control circuit, a UV sensor is used to monitor the radiant power of the lamp. In a control unit, the signal is compared with a preset signal or with a signal provided by a tachometer. The resulting difference in the signal is magnified and used to control the lamp current by transductor or thyristor switches.[24] An example of a control system is in Figure 3.11.
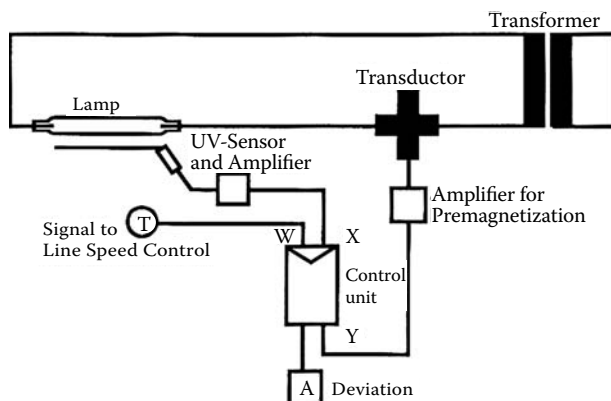


**FIGURE 3.11**
Example of a control system for a mercury lamp. (Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, SITA Technology Ltd. p. 66 (1998). With permission from SITA Technology Ltd.)

Recently electronic control systems for power supplies have been developed. Their reported advantages over conventional systems are:[25]

- Current or power controlled system, independent of main voltage
- Electrical efficiency over 92%
- No external electrical compensation necessary
- Very low adjustable standby power (<40%)
- Large dimming range (15 to 110%)
- Compact dimensions and lower weight

This type of control system is operated at medium frequency and is currently limited to a maximum power of about 5 kW.[24]

## 3.2 Electron Beam Curing Equipment

Commercial electron beam processors available today vary in accelerating voltage range from about 100 kV up to about 10 MV. The original development of electron beam technology in the 1950s concentrated on machines with accelerating voltages in the range from 1 to 2 MV with beam powers of 5 to 10 kW, suitable primarily for the cross-linking of plastic materials. During the 1960s, the successful applications required even higher voltages, up to 3 and 4 MV, with power output levels up to 100 kW.[25] Lower-voltage machines in the range below 300 kV were developed in the 1970s. They were designed without a beam scanner, which was used in the higher-voltage equipment. The electron beam in the lower-voltage range was delivered as a continuous "shower" or "curtain" across the entire width of the product. The main applications of the lower-voltage machines were coatings and other thin-film layers.[25] The most recent designs use voltages in the range of 70 to 125 kV, with electron energies suitable for the processing of thin layers of inks and lacquers less than 25 microns thick.

The principle of producing high-energy electrons is very simple. The electrons are emitted in a vacuum by a heated cathode and accelerated in the electrostatic field applied between cathode and anode. Acceleration takes place from the cathode, which is connected to a negative high-voltage potential, to the grounded accelerator window as anode. Usually an electron optical system is used to focus the accelerated electrons to the accelerator window plane.

The energy gain of the electrons is proportional to the accelerating voltage. It is expressed in electron volts (eV), i.e., the energy that a particle of unit charge gains by passing a potential difference of 1 V. The electrons leave the vacuum chamber and reach the process zone if their energy is high enough
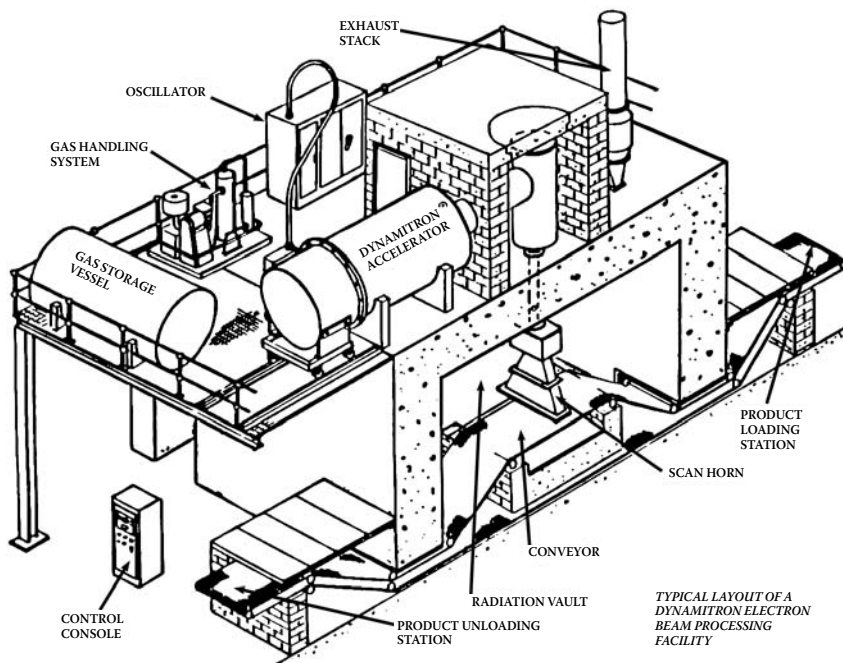
**FIGURE 3.12**

Traditional design of a high-energy EB unit. (Bly, J.H., *Radiat. Phys. Chem.* Vol 14, p. 41 (1979). With permission from Elsevier Ltd.)

to penetrate the 6 to 14 µm thick titanium window foils used in the lower-energy range and 40 to 50 µm thick foils used in the higher-energy range.

As pointed out in Section 2.2, stopping the high-energy electrons by a material generates x-rays. For that reason, the electron accelerator and process zones have to be shielded to protect the operator. For electrons with energies up to 300 keV, a self-shielding with lead cladding up to about 1 in. thick is sufficient. For systems where electrons with higher energy are generated, the equipment is shielded by a concrete or steel vault built around it, as shown in Figure 3.12.

The basic electrical parameters of an electron beam processor are its *acceleration voltage*, the *electron beam current*, and the *electron beam power*. The ratio of electron beam power and the input electrical power defines the efficiency of an electron accelerator.[26] The acceleration voltage determines the energy of the electrons, as pointed out in Section 2.2.

The absorption properties of the accelerated electrons in the processed materials are the *absorbed dose*, the *depth dose profile*, the *penetration range*, and the *dose rate*.

Process parameters involve line speed; if dose rate and line speed are combined, the dose delivered to the product to be cured can be calculated. A processor specific yield factor depends on the relationship between the beam current

and line speed. The *dose-speed capacity* of a processor is given by the product of the line speed and the delivered dose at maximum electron beam power.[27]
  The above-mentioned parameters are defined below:

*Acceleration voltage*: Potential difference between cathode and anode of the accelerator, usually expressed in kV or MV and obtained using a resistive voltage divider chain in the high-voltage unit.

*Electron beam current*: Number of electrons per second emitted from the cathode, measured in mA (1 mA = $6.25 \times 10^{15}$ electrons per second) at the high-voltage unit.

*Electron beam power*: Product of the acceleration voltage and the electron beam current, expressed in kW (1 kW = 10 mA × 100 kV or 10 mA × 0.1 MV).

*Absorbed dose*: Mean value of energy of the ionizing radiation absorbed by the unit of mass of the processed material. The unit of absorbed dose is 1 Gray (Gy) = 1 J kg$^{-1}$ or 1 kGy = 1 J g$^{-1}$. The older unit, used officially until 1986 and still used occasionally in literature, is 1 megarad (Mrad), which is equivalent to 10 kGy.

*Depth dose profile*: The energy deposition produced by electrons of a given energy in an absorber can be expressed as a function of depth, density, atomic number, and atomic weight of the absorber. The energy loss dE/dx of the fast electrons (expressed in MeV cm$^{-1}$) is given as a function of the mass per unit of area (g cm$^{-2}$), which is equivalent to the depth in cm times the density in g cm$^{-3}$. It is directly proportional to the absorbed dose: $1/\rho$ dE/dx = dose × unit area, with dimensions J g$^{-1}$cm$^2$. In realistic electron beam processes, energy losses occur in the titanium window foil, in the air gap between foil and the coating, and in the substrate.

*Dose rate*: Dose per unit time, expressed in Gy s$^{-1}$ = J kg$^{-1}$s$^{-1}$. At a constant accelerating voltage, it is proportional to the electron beam current.

*Line speed*: Speed of the material being irradiated, usually expressed in m/min or ft/min. It determines the exposure time of the material.

*Delivered dose*: The ratio of the dose rate and the line speed:

$$\text{Delivered dose} = \text{Dose rate}/\text{Line speed}$$

At a given dose rate, the line speed can be adjusted to obtain the desired dose. On the other hand, the beam current can be controlled by the line speed to maintain a constant delivered dose at all line speeds.

*Yield factor*: Yield factor is used to characterize the curing performance of an electron processor. It is a constant that relates the delivered dose to the beam current and line speed:

$$\text{Delivered dose} = \text{Yield factor} \times \text{Beam current/line speed}$$

The unit of yield factor is kGy × m/min/mA.

*Dose-speed capacity*: Product of the delivered dose and the line speed at the maximum beam power:

Dose-speed capacity = Delivered dose × Line speed

In usual EB operation, the dose-speed capacity is measured in m/min at 10 kGy. It is the most convenient unit to relate the curing performance of an electron beam processor to the desired process parameters, such as dose and line speed.[28]

## 3.2.1 Particle Accelerators

Particle accelerators produce electrically charged particles with speeds slightly over 6,000 miles/s to speeds approaching the speed of light. Accelerated particles are generally formed into a beam and directed at a material called a beam window. The window is thin enough so that the particle beam may pass through it without much energy loss. As this beam passes through the window material, some of the particles are deflected and may interact with atomic nuclei. The final effect depends on the energy and nature of the incident particle. A particle accelerator is depicted schematically in Figure 3.13.[29]

There are several designs of accelerators for industrial use. They are mainly used to accelerate electrons, although they can be adapted to accelerate ions
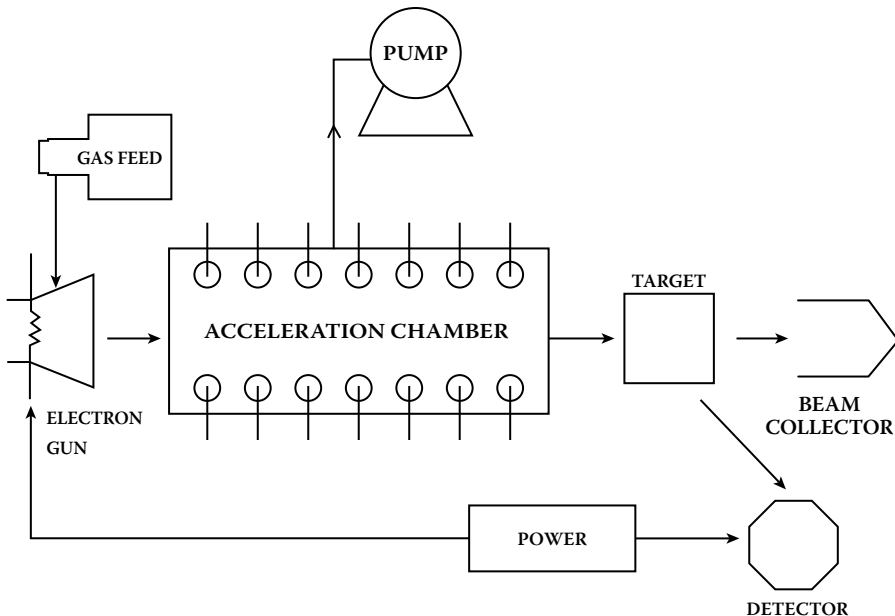


**FIGURE 3.13**
Schematic of a particle accelerator.

as well. For the purpose of this publication, the accelerators of electrons will be discussed at some length.

Essentially, there are two types of electron accelerators used in industrial electron beam applications. *Direct accelerators*, also referred to as *potential drop accelerators*, require the generation of high electrical potentials equal to the final energies of the accelerated electrons. *Indirect accelerators* produce high electron energies by repetitive application of time-varying electromagnetic fields.[30] Direct accelerators are widely used for low- and medium-energy applications since they are able to provide continuous electron beams with high average current and power ratings, which translate to high processing rates. For higher energies (about 5 MeV), indirect accelerators using microwave radiation, very high-frequency (VHF) radiation, or pulsed electrical power are considered to be more suitable. Modern accelerators can generate beam powers up to several hundred kilowatts and electron energies up to 15 MeV.[30]

### 3.2.1.1 Direct Accelerators

In principle, a direct electron accelerator consists of a high-voltage generator connected to an evacuated acceleration system. The different direct accelerators currently used employ similar methods for electron emission, acceleration, and dispersion; the differences are in the design of their voltage generators.

The source of electrons is a thermionic cathode, which is almost always a tungsten or thoriated tungsten wire, although tantalum wire or lithium hexaboride pellets are also used as cathodes.[30] Electron emission is most frequently controlled by the variation of temperature of the cathode, but this can be done also by a grid with variable voltage. The beam of electrons is extracted, focused, and accelerated by an internal electric field, determined by a series of electrodes or dynodes with intermediate potentials obtained from a resistive voltage divider.[30] The electrons gain energy continuously throughout the length of the acceleration tube. After acceleration, the concentrated electron beam is dispersed by scanning with a time-varying magnetic field with a sweep rate of at least 100 Hz. The divergent beam so formed expands within an evacuated scan horn and then emerges into the air through a thin metallic foil. This foil is usually made from titanium, but other metals, such as aluminum alloys or titanium alloys, are used.[30] In order to minimize the loss of the electron energy, the thickness of a titanium foil is kept in the range between 25 to 50 μm for electron energies above 0.5 MeV and between 6 and 15 μm for energies below 0.3 MeV. The windows of the scanning horn may be as wide as 2 m (80 in.).[30]

#### 3.2.1.1.1 Electrostatic Generators

Electrostatic generators are based on the principle that high electric potentials can be produced by mechanically moving static charges between low-voltage and high-voltage terminals. The various designs have used endless rubber belts, chains, or metallic electrodes with insulating links,
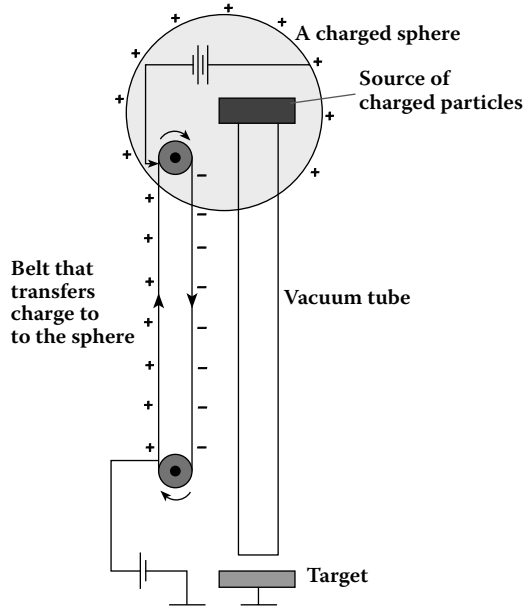
**FIGURE 3.14**
Schematic of the Van de Graaff accelerator.

and rotating glass cylinders. Compressed gasses, for example, nitrogen, sulfur hexafluoride ($SF_6$), Freon, carbon dioxide, and others, are used for high-voltage insulation to reduce the size of the equipment. One example of such a device is a Van de Graaff generator (Figure 3.14), a belt-driven machine, originally developed in the 1930s for research in nuclear physics. Industrial versions capable of delivering several kW of electron beam power with energies up to 4 MeV were developed in the 1950s. They were used for electron beam cross-linking of plastic films, tubing, and insulated wire, and biomedical applications.[31] Today, these machines are no longer competitive with modern high-power machines and are therefore seldom used in industrial applications.

### 3.2.1.1.2 Resonant Transformers

Pulsed electron beams produced by these devices are generally limited to an average current of about 5 to 6 mA since they operate at a relatively low frequency of 180 Hz. The voltage of such an accelerator is not rectified as it is in other industrial accelerators, and the high voltages (typically 1.0 and 2.0 MV) of commercial resonant transformers produce pulsating current at their resonant frequency. This pulsating current makes it difficult to achieve a uniform dose in the irradiated material. These machines consist of a pressure tank, in which the iron-free resonant transformer and the discharge tube are placed.

Secondary windings connected in series feed the high-voltage terminal. The system provides a beam only during the negative half cycle, with a voltage variation between zero and the peak value the machine was designed to deliver. Sulfur hexafluoride gas is used for electrical insulation.[32]

### 3.2.1.1.3 Iron Core Transformers

Low-frequency transformers with iron cores connected to rectifier circuits can generate potentials up to approximately 1 MV. Traditionally, iron core transformers are insulated by oil, but the recent models use sulfur hexafluoride. The energy rating of these generators is in the range from 0.3 and 1 MeV with beam powers up to 100 kW.[33,34]

### 3.2.1.1.4 Insulating Core Transformers

Insulating core transformers (ICTs) were developed in the late 1950s and early 1960s to replace Van de Graaff electrostatic generators to provide more irradiation power for higher processing rates. An ICT consists of a three-phase transformer with multiple secondary windings that are energized serially by iron core segments. These segments are separated by thin sheets of dielectric material. Low-voltage, low-frequency AC power is converted into high-voltage DC power by using rectifier circuits connected to the nearest core segment. This way the electrical stresses in the system are minimized. ICT designs are capable of higher-voltage ratings than conventional iron core transformers.[33] The insulating medium is sulfur hexafluoride gas, and the line-to-beam power efficiency is close to 85%.[35–38] The terminal voltage of the ICT power supply is connected to an accelerator tube. The electron beam for industrial applications starts from a tungsten filament and is accelerated within the evacuated tube as in other DC accelerators.

ICT machines produced recently have energy ratings from 0.3 to 3.0 MeV and beam power capabilities up to 100 kW. Nearly 180 of these machines, the majority of them rated for less than 1 MeV, have been installed as of the early 1990s. They are used mainly for cross-linking of heat-shrinkable film, plastic tubing, and electric wire.[33]

### 3.2.1.1.5 Cockcroft-Walton Generators

This is essentially a cascade generator. In this type of electron accelerator, the high voltage is produced by the incremental movement of electric charge. The high-voltage system is a condenser-coupled, cascade rectifier, which converts low-voltage, medium-frequency (3 kHz) AC power into high-voltage DC power. The capacitive coupling circuits are connected in series. Sulfur hexafluoride is used as insulation.[39] Cockcroft-Walton generators are made in different designs. Three-phase rectifier circuits are used for low-energy, high-current applications, conventional single-phase cascades for energies between 1 and 3 MeV, and balanced two-phase systems for energies between 1 and 5 MeV with beam power ratings up to 100 kW. Electrical efficiencies are about 75%.[40]

Vessel Cooler

RF Transformer

High Voltage
Terminal

RF Electrode

RF Oscillator

Electron Gun

Acceleration Tube

Corona Rings

Rectifier
Modules

Vacuum
Pumps

Pressure Vessel

Scan Chamber

Scan Horn

Window

Window
Cooling
Manifold
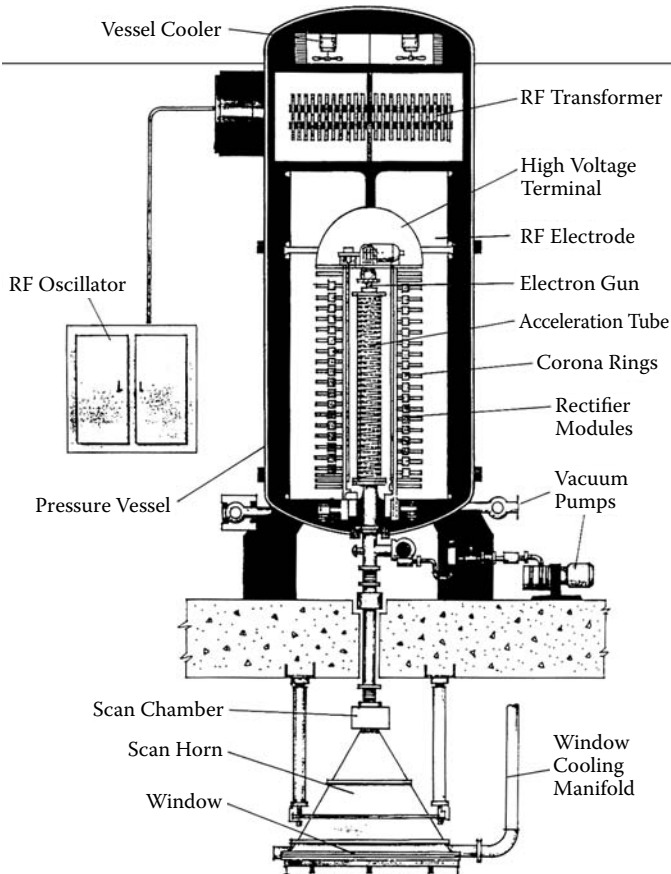
**FIGURE 3.15**
Schematic of a direct accelerator (Dynamitron) accelerator. (Courtesy of IBA.)

### 3.2.1.1.6 *Dynamitrons*

In the Dynamitron type of accelerator (Figure 3.15), the high-voltage DC power is generated by means of a cascade rectifier circuit energized by high-frequency (100 kHz) AC power. The rectifiers are driven in parallel by a pair of large semicylindrical electrodes, which surround the high-voltage column. This arrangement enhances the reliability at the maximum voltage by eliminating the large, high-voltage condensers used in a series-coupled Cockcroft-Walton generator. Because of power loss in the high-frequency oscillator, employing a triode vacuum tube, the electrical efficiency of a Dynamitron accelerator is about 60%.[41,42] These machines have been made with energy ratings from 0.5 to 5 MeV and beam power ratings up to 250 kW. More than 150 Dynamitrons, the majority of which having energy ratings above 1 MeV, are used for the cross-linking of polymeric materials.[33] Some of the larger

machines with energy ratings above 3 MeV are also used for sterilization of medical products by energetic electrons.[43] The largest model, which can deliver 250 kW of beam power at energies in the range from 3 to 5 MeV, is equipped with a high-power target for x-ray processing.[44,45]

### 3.2.1.2  Indirect Accelerators

This type of accelerator produces high-energy electrons by injecting short pulses of low-energy electrons into a copper waveguide, which contains intense microwave radiation. When the injection phase is at its optimum, the electrons are able to gain energy from the alternating electromagnetic field. Their final energy depends on the average strength of the field and the length of the waveguide.[46] Such an accelerator is referred to as a *microwave linear accelerator*, or *linac*, and is the most prevalent type of indirect accelerator.[46] It is shown schematically in Figure 3.16.

Linacs operate with much lower average beam current and power levels than most DC accelerators to attain sufficiently high electron energy. The relatively low voltage of the microwave component and the use of a grounded copper waveguide result in smaller size when compared to DC machines with the same electron energy. Their disadvantage is a low overall electrical efficiency ranging from 20 to 30%.[47]

Low-power linacs are mostly used in cancer therapy and industrial radiography, whereas medium-power linacs are utilized in radiation processing.



**TRAVELING–WAVE LINEAR
ELECTRON · ACCELERATOR**
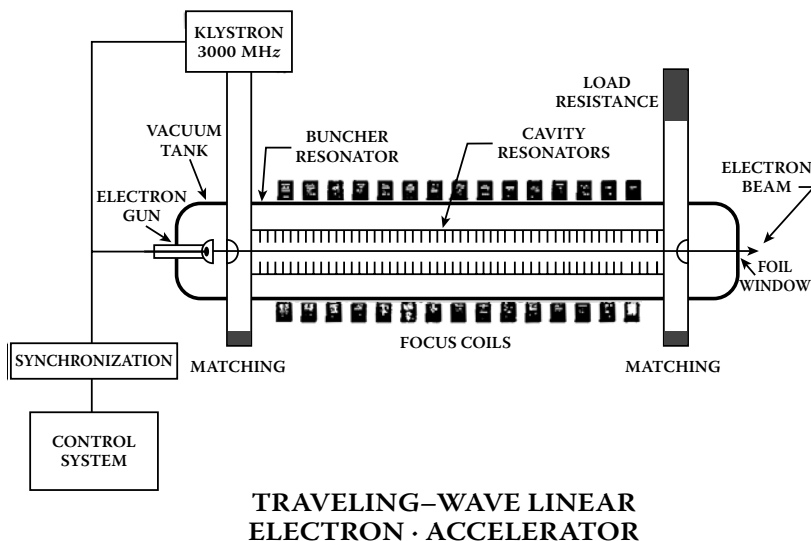
**FIGURE 3.16**
Schematic of an indirect accelerator (microwave linac). (Clelland, M.R., *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.) Carl Hanser Publishers, p. 30 (1992). With permission of Carl Hanser Publishers.)

### 3.2.1.2.1 Traveling Wave Linacs

In traveling wave (TW) linacs, the microwave power is injected in one end of the waveguide and propagates to the other end. At that point, any residual microwave power is dissipated in a resistive load. Low-energy electrons are also injected with the microwave power and travel along in step with the moving electric wave, gaining energy from it continuously.

The peak microwave power must be several MW in order to obtain energy gains of several MeV per meter, and the system must be operated in short, repetitive pulses to keep the average microwave power down to reasonable levels. The electron beam current during the pulse ranges from 0.1 to 1.0 A for an average beam power of 10 to 20 kW at the electron energy of 10 MeV.[48] Although with optimal beam current, TW linacs can transfer microwave power with an efficiency ranging from 80 to 90%,[49] because of the low efficiency of the microwave generation in a klystron, the overall line-to-beam power efficiency is usually below 30%.

### 3.2.1.2.2 Standing Wave Linacs

A standing wave (SW) microwave linear accelerator consists of a linear array of resonant cavities that are energized by a common source of microwave power. These cavities are nearly isolated by webs with small-diameter apertures, and the high-energy electron beam passes through these apertures. However, they are coupled through intermediate cavities, which stabilize the microwave phase relationship between the accelerating cavities.

SW linacs have higher electrical impedance or quality factor (Q) than TW linacs with similar energy and beam power ratings.[50] This can provide higher energy gain for the same length of waveguide or a shorter waveguide for the same energy gain, which is an advantage if the accelerator for the given application needs to be compact.

### 3.2.1.2.3 Resonant Cavity Accelerators

Resonant cavity accelerators consist of several resonant cavities in series energized by a single S-band klystron using a microwave power distribution system.[51] Another system consists of a single VHF cavity energized by a triode tube that is less expensive than a klystron. The resonant frequency of the latter is about 110 MHz, which is well below the microwave range.[52] Resonant cavity accelerators with electron energies of a few MeV are useful for irradiating thin polymeric products such as heat-shrinkable tubing and electrical wire.[53]

### 3.2.1.2.4 Linear Induction Accelerators

A linear induction accelerator (LIA) accelerates electrons by a series of single-turn, toroidal pulse transformers through which the beam passes. The energy gain in each stage is equal to the voltage applied to the primary winding. The beam acts as a secondary winding. The electrical impedance

of a linear induction accelerator is very low. This makes it suitable for accelerating high-peak beam currents. In principle, the electrical efficiency of this accelerator can be substantially greater than that of a microwave linac.[54]

Detailed information on designs, principles of operation, and performance characteristics of electron accelerators is available in several books.[35,36,55,56]

### 3.2.1.2.5 Rhodotron Accelerators

A Rhodotron is an electron accelerator based on the principle of recirculation of a beam in successive passes through a single coaxial cavity resonating in the VHF frequency range. This large-diameter cavity operates with a relatively low microwave field, which makes it possible to achieve continuous wave (CW) acceleration of electron beams to high energies.

Rhodotron cavities are shaped as coaxial lines shorted on both ends and resonating in the half-wavelength mode 107.5 or 215 MHz. The beam crosses the diameter of the cavity in the median plane through successive passes (see Figure 3.17).[57] External dipole magnets are used to bend back the electrons emerging from the cavity and redirect them toward the cavity center. A high-power radio frequency (RF) system using a tetrode tube produces the electric field, allowing an energy gain of 0.83 to 1.17 MeV per crossing. Ten or twelve crossings of the cavity (which means nine or eleven bending magnets) are therefore required to obtain 10 MeV electron beams at the exit of this accelerator. A very high-power version can produce a 100 mA beam at 5 to 7 MeV with six passes. With this version, the average electron beam power is in the range of 500 to 700 kW, which can be used for producing intense x-ray (*bremsstrahlung*) beams. Since the electrons travel along a rose-shaped path (see Figure 3.17), the name Rhodotron was chosen derived from Greek word *rhodos*, which means "rose."[57]
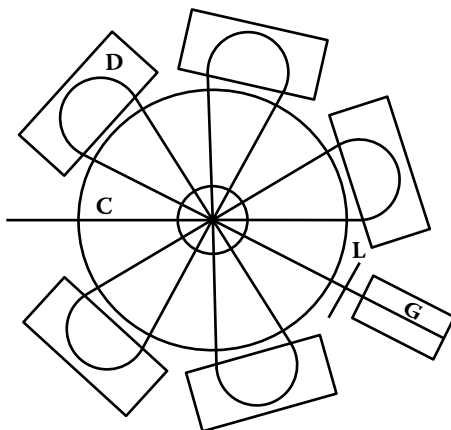


**FIGURE 3.17**
Schematic of a Rhodotron accelerator. (Courtesy of IBA.)
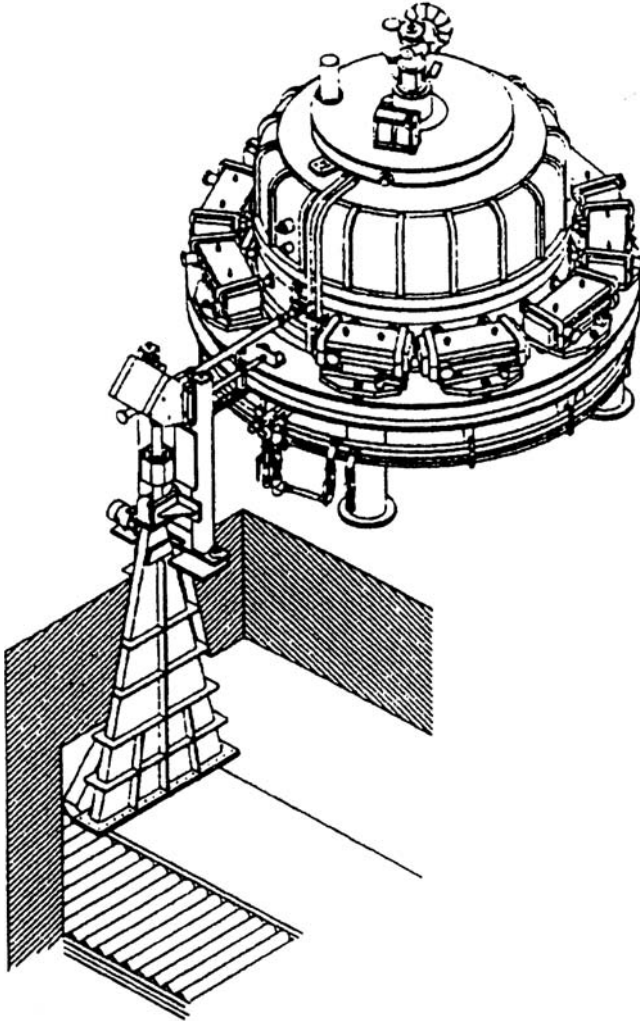
**FIGURE 3.18**
An example of a Rhodotron system with a scanning horn. (Courtesy of IBA.)

The electron gun is located at the outer wall of the accelerating cavity, and the electrons are injected into the cavity at a voltage of about 35–40 kV. The cavity is cooled by a water jacket on the inner coaxial conductor and at the end flanges and by discrete water channels along the outer diameter. The system is designed to operate with a 2 MW cooling tower up to an outside temperature of 35°C (95°F). Therefore, no water chiller is required.[57] The RF amplifier detects and follows changes in the resonant frequency of the cavity so that accurate control of the cavity temperature is not required.

The electron beam is of very high quality with low energy spread and low angular divergence.[58] This simplifies the design and operation of external beam transport and scanning systems.[59] The beam delivery system includes a scanning horn with a vacuum-to-atmosphere window using a thin metal foil. An example of a Rhodotron with a scanning horn is in Figure 3.18.

The control system is based on an industrial programmable logic controller (PLC). It includes all software required for the completely automatic operation, maintenance, and troubleshooting of the accelerator.[57]

In addition to providing electron beams with 5 and 10 MeV electron energy outputs for usual EB applications, Rhodotron can be used to produce *bremsstrahlung x-rays* from a metallic target that can be used for industrial applications.[57,60–62] Rhodotron is particularly suitable for applications that need a powerful beam (30–200 kW) in the energy range of 1 to 10 MeV.[63]

### 3.2.1.3  Low-Energy Electron Accelerators

Electron accelerators discussed in Sections 2.1 and 2.2 are generating high-energy electrons (10 MeV or even more) and are used mainly to process thick polymeric products, typically up to 20 mm, and for sterilizing medical devices and food processing. However, the vast majority of current industrial irradiation work, such as cross-linking of thin polymeric films and sheets, polymerization, and cross-linking of coatings, is done by low- to moderate-energy accelerators with low electron energies (less than 1.0 MeV).[64] Low-energy accelerators are used, often as reliable computer-controlled subsystems, in coating lines, printing presses, laminating machines, etc. Their operating parameters, such as electron energy, electron beam power, irradiation width, and delivered dose rate, can be matched to the demands of the given industrial process. Such machines are often referred to as *electron processors.* The three most common designs of industrial low-energy electron accelerators are shown in Figure 3.19.

The selection of a suitable electron processor type is dictated by the process parameters. *Scanning* type electron accelerators use a typical small-diameter electron gun, which generates and shapes a pencil beam. The beam is deflected over the window area by using periodically changing magnetic fields. Carefully tuned deflection produces a very uniform beam current (or dose rate) distribution across the beam exit. Energies up to 1.0 MeV can be reached at medium to high beam current. Due to limited deflection angle, the length of the scanning horn must be somewhat larger than the length of the exit window.

*Single-filament design*, consisting of a long linear filament to determine the beam current and beam width, eliminates the need for a beam scanning system. Since the current extractable from a unit length of the single filament is limited, multifilament cathode configurations are often used. This also improves the uniformity of the beam current distribution, which is usually less homogeneous than that obtained in scanning horn processors.[65] The beam width is limited by the necessity to span the filament across the full

Scanned Beam  Single Linear Filament  Multiple Filament
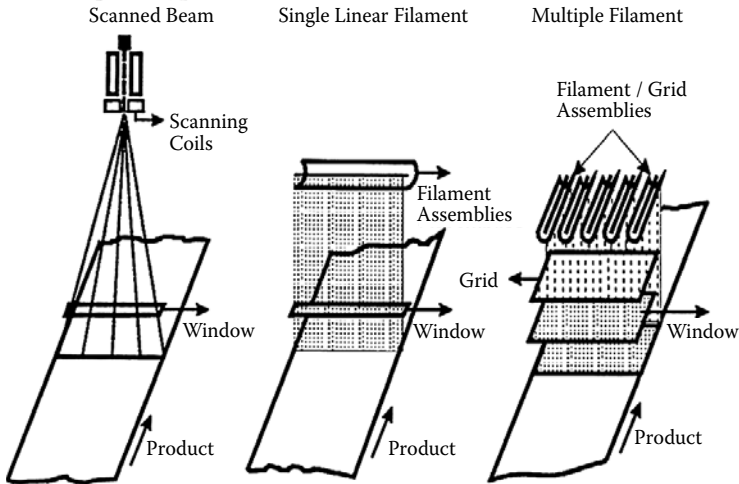
**FIGURE 3.19**
Common designs of industrial low-energy accelerators. (Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, SITA Technology Ltd., p. 138 (1998). With permission from SITA Technology Ltd.)

width of the exit window to a maximum of about 2 m (80 in.). This design is no longer used on currently made machines.

*Multifilament design*, consisting of an assembly of short, about 20 cm (8 in.) long, filaments set parallel to the web direction, eliminates the problem of filament support and adjustment of the single-filament design. The filaments are mounted between two rigid bars determining the length of the filament assembly. A control and screen grid define the electron optical extraction conditions for each filament into a single gap accelerator. The overlapped beams emitted from adjacent cathode filaments form a uniform electron cloud before the acceleration takes place. This design is capable of generating high beam power, dose uniformity, and a wider beam than the single-filament design.[65]

### 3.2.1.3.1  Single-Stage Scanned Beam Accelerator

The accelerator for the electron beam processor produced by Electron Crosslinking AB in Halmstadt, Sweden, originally developed by Polymer Physik in Tübingen, Germany, uses a classical triode system as electron gun, a single electrode gap, and a beam focusing and deflection system. The acceleration voltage depends on the application and ranges from 150 to 300 kV.[66] The processor is shown in Figure 3.20.

The electron gun consists of a spiral-shaped tungsten cathode and a Wehnelt cylinder. These two components not only constitute the electrodes of the acceleration gap, but also form the optical assembly to control and shape the electron beam. Current signals are linear and have a repetition frequency
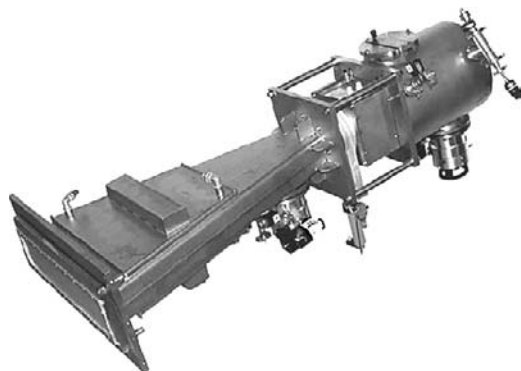
**FIGURE 3.20**
Single-stage scanned beam accelerator with a range of accelerating voltages from 80 to 300 kV.
(Courtesy of Elektron Crosslinking AB.)

of about 800 Hz. They are used to deflect the electron beam horizontally and
vertically over the exit window plane. The scanner may be equipped by two
cathodes for maximum output. Then, the width of the exit window is more
than double that of a standard unit with a single cathode. The exit window
containing the 12 to 15 μm thick titanium foil is relatively large to ensure an
effective cooling of the foil.

Nissin High Voltage Co. of Japan also offers machines with electron scan-
ners. The acceleration voltages in these machines are in the 300 to 500 kV
range with beam powers up to 65 kW. The maximum beam width is 1,200
mm (48 in.).[67] An example of a machine of this type is in Figure 3.21.

### 3.2.1.3.2  Linear Cathode Electron Accelerators

Linear cathode accelerator employs a cylindrical vacuum chamber in which a
longitudinal heated tungsten filament cathode is raised to the negative accel-
erating potential. The electrons emitted from the cathode are accelerated in
a single step to the exit window. The exit window as a part of the vacuum
chamber is kept at ground potential. The accelerated electrons penetrate the
thin titanium window and enter the process zone. A linear cathode proces-
sor using a single filament has a dose-speed capacity of about 450 m/min
(1,500 ft/min) at 10 kGy. In the actual commercial equipment, the cathode
assembly contains up to four filaments, which are capable of providing a dose-
speed capacity of up to 1,350 m/min (4,500 ft/min) at 10 kGy or a beam current
of several hundred mA.[67] The processor is supplied with a protective shielding
against x-rays in the form of a lead slab. The x-ray shielding and product han-
dling system are designed to match the specific process demands.

The process control is provided by programmable process controllers
(PLCs), which are flexible and upgradable. The addition of man-machine
interfaces (MMIs) based on personal computers and common software
systems allows not only system control and interlocks, but also a history
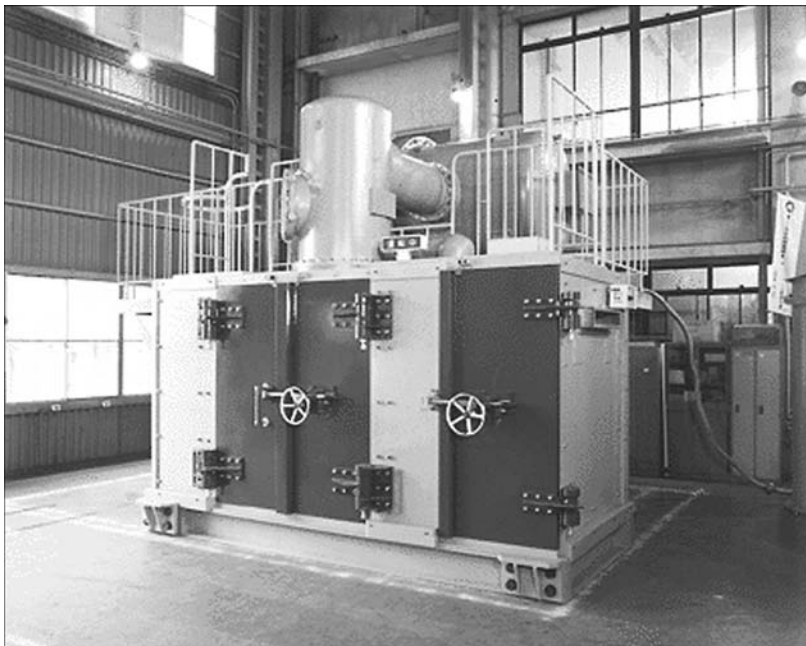
**FIGURE 3.21**
Self-shielding EB processor with the accelerating voltages of 800 kV. (Courtesy of Nissin Electric.)

of operation, communication, and archiving.[68] A series of processors of this design were manufactured by Energy Sciences, Inc. in Wilmington, Massachusetts, under the brand Electrocurtain® in the 1970s and 1980s.

Another low-energy processor can be described as a vacuum diode operating in the current saturation mode; i.e., the cathode is a directly heated tungsten filament without a control grid. The electrons emitted from the cathode are shaped into electron beam bundles by a forming electrode and accelerated to the exit window. This diode configuration ensures that practically all electrons emitted are accelerated. Cathode heating can be accomplished through the high-voltage cable. This allows moderate electron currents at low heating power.[69] An example of such a processor was EBOGEN, produced by igm Robotersysteme in Munich, Germany (Figures 3.22 and 3.23). At this writing the equipment has been reportedly modified and is produced by Steigerwald Strahltechnik in Maisach, Germany, under the trade name EBOCAM®. It is used mainly for welding and drilling metals.

### 3.2.1.3.3 Multifilament Linear Cathode Electron Accelerators

In this design, a multiple emitter assembly with heated tungsten filaments placed in parallel to the product's direction is used. The beam current is controlled by molybdenum grids held at a common potential. A planar screen
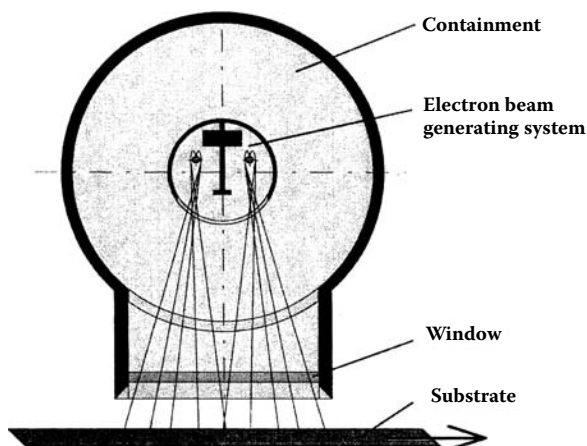
**FIGURE 3.22**
Schematic of the processor EBOGEN. (Courtesy of igm Robotersysteme.)

grid is placed below the control grids. In the field-free region between the grids, a highly uniform electron density is generated prior to acceleration. The acceleration of electrons occurs between the planar screen grid and the grounded window. This design is represented by the BROADBEAM™ processor that was manufactured by the now defunct RPC Industries in Hayward, California. Currently, this type of equipment (Figure 3.24) is produced by PCT Engineered Systems in Davenport, Iowa.



**FIGURE 3.23**
EBOGEN processing unit. (Courtesy of Igm Robotersysteme.)
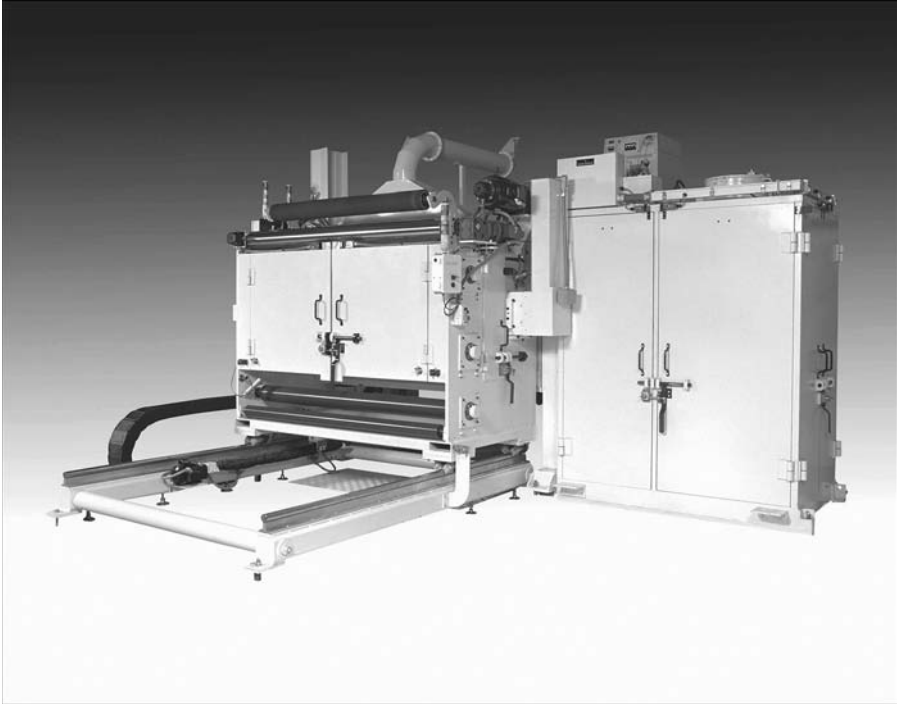
**FIGURE 3.24**
BROADBEAM processor. (Courtesy of PCT Engineering Systems.)
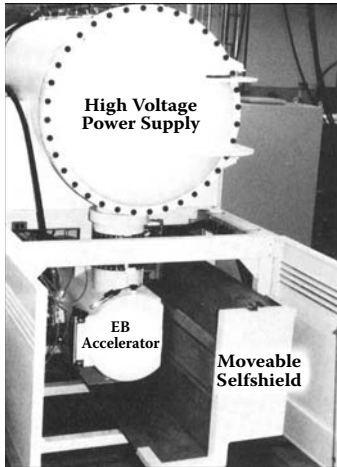


**FIGURE 3.25**
Low-energy self-shielding electron beam processor. (Courtesy of Energy Sciences, Inc.)

**TABLE 3.2**

General Operating Characteristics of Commercial Low-Energy Industrial Electron
Beam Processors

| Processor | Electrocurtain | BROADBEAM | EBOGEN | Polymer Physik |
|---|---|---|---|---|
| Acceleration voltage, kV | 150–300 | 150–300 | 120–150 | 150–300 |
| Working width, mm | 150–2,000 | 300–2,500 | 3300-1400 | 150–2,000 |
| Web speed at 10 kGy, max., m/min | 1,350 | 1,500 | 450 | 1,350 |
| Dose variation across the web, % | ±10 | ±5 | ±12 | ±10 |

*Source:* Korenev, S., *Radiat. Phys. Chem.*, 71, p. 535 (2004).

The operating characteristics of the four most widely used low-energy
electron beam processors are in Table 3.2.

A new window design (cooling and support structure) combined with a
multifilament cathode arrangement led to the development of low-energy,
low-cost electron processors, such as Electrocure™ and EZ Cure™ manufac-
tured by Energy Sciences, Inc., Wilmington, Massachusetts (Figure 3.25.). For
example, a 150 kV processor is capable of a dose-speed capacity of 1,200 m/min
(3,950 ft/min) at 10 kGy. An even more powerful 125 kV, 200 kW processor is
capable of curing coatings on a web 1,650 mm (66 in.) wide with a dose-speed
capacity of 2,250 m/min (7,400 ft/min) at 10 kGy.[70,71] Smaller, lower-voltage pro-
cessors operating between 90 and 110 kV accelerating voltages are capable of
speeds up to 400 m/min (1,310 ft/min).[71]

### 3.2.2 Recent Trends in Development of EB Curing Equipment and Technology

Current developments in the electron beam curing technology include:

- Lowering equipment cost
- Reducing size and weight of the curing equipment
- Eliminating or reducing the use of nitrogen inerting

Lowering accelerator voltage is the single major factor helping to meet the
above requirements. Lower accelerating voltage means a less expensive power
supply, smaller size accelerator head, and less x-ray shielding.[72] For example,
a newly designed 75 kV MicroBeam-LV processor (Energy Sciences, Inc.)
(see Figure 3.25) is capable of curing coatings up to 0.001 in. (25 μm) thick (at

**TABLE 3.3**

Comparison of Standard and Low-Voltage EB Processors for a 48 In. Wide Web

| Dimensions | Standard Processor | Low-Voltage Processor |
|---|---|---|
| In-line dimensions, ft (mm) | 7 (2,135) | 4.5 (1,370) |
| Height, ft (mm) | 10 (3,050) | 4.5 (1,370) |
| Depth, ft (mm) | 12 (3,660) | 6 (1,830) |

*Source:* Maguire, E. F., *RadTech Report*, 12, No. 5, RadTech International N.A., p. 18 (1998). With permission from RadTech International N.A.

density 1). Complete cure is achieved at doses 1–2.5 Mrad (10–25 kGy), which is considerably lower than the typical 3 Mrad (30 kGy) required for the 150 kV equipment. Compared to a standard processor, the total volume is 50% smaller. Comparison of standard and low-voltage processors for 48 in. wide web is in Table 3.3.[73] PCT Engineered Systems is offering the BROADBEAM LE Series with accelerating voltages in the range from 70 to 125 kV, to be used in coil coating, web offset presses, flexo presses, laminating presses, and specialty cross-linking, with throughput typically 30 kGy at 400 m/min (1,312 ft/min).

The penetration depth of electrons into the substrate decreases at lower energy. Also, the surface dose per mA of beam current increases (see Figure 3.26) and thin coatings and inks can be cured with higher efficiency



**FIGURE 3.26**
Miniature electron beam processor (gun and power supply). (Courtesy of Ushio America.)

and speed. The higher surface dose produces a higher concentration of radicals, which in turn reduces the oxygen inhibition.[71]

Relatively recent developments are electron generators that are essentially sealed vacuum tubes with a 2.5 µm thick silica ceramic window or a 6 µm titanium window as the beam exit. Such electron beam tubes or bulbs are capable of operating at 50 to 150 kV[71,74–78] and can be connected into modules to cure wide webs. It is conceivable that miniature electron beam tubes may provide efficient low-cost means to cure thin coatings, inks, and adhesives, thus offering an alternative to irradiation by UV lamps. A schematic of the patented emitter is in Figure 3.27a, and an actual 10 in. emitter is in Figure 3.27b.

A review of reactor design concepts by Berejka is in Reference 79.



(a)
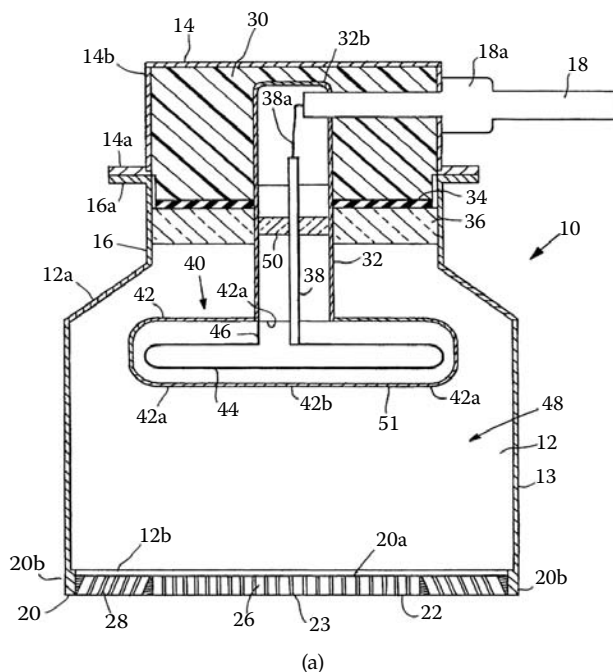
**FIGURE 3.27**
(a) Schematic of a low-voltage electron beam emitter (U.S. Patent 6,545,398). (b) Low-voltage 10-in. emitter. (Courtesy AEB, Inc.)

(b)

**FIGURE 3.27**
(Continued)

## References

1. Berejka, A. J., in *Conference Proceedings, 3rd Annual Green Chemistry and Engineering* (June 29–July 1, Washington, DC), p. 35 (1999).
2. Stowe, R. W., *RadTech Europe '97, Conference Proceedings*, (June 16–18, Lyon, France), p. 603 (1997).
3. Davidson, R. S., *Exploring the Science, Technology and Applications of UV and EB Curing*, SITA Technology Ltd., London, p. 13 (1999).
4. Knight, R. E., in *Chemistry and Technology of UV and EB Formulations for Coatings, Inks and Paints*, Vol. 1 (Oldring, P. K. T., Ed.), SITA Technology Ltd., London, p. 159 (1991).
5. Davidson, R. E., *Exploring the Science, Technology and Applications of UV and EB Curing*, SITA Technology Ltd., London, p. 16 (1999).
6. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology Ltd., London, p. 73 (1998).
7. Davidson, R. E., *Exploring the Science, Technology and Applications of UV and EB Curing*, SITA Technology Ltd., London, p. 17 (1999).
8. Roth, A., *RadTech Europe '97, Conference Proceedings* (June 16–18, Lyon, France), p. 91 (1997).
9. Eliasson, B., and Kogelschatz, U., *Appl. Phys.*, B46, p. 299 (1998).
10. Kumagai, H., and Obara, M., *Appl. Phys. Lett.*, 54, p. 2619 (1989).
11. Skinner, D., *RadTech Europe '97, Conference Proceedings*, (June 16–18, Lyon, France), p. 133 (1997).
12. Roth, A., *RadTech Report*, 10, No. 5, September/October, p. 21 (1996).
13. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology Ltd., London, p. 95 (1998).
14. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology Ltd., London, p. 102 (1998).
15. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology Ltd., London, p. 101 (1998).
16. Whittle, S., *RadTech Report*, 14, No. 1, January/February, p. 13 (2000).
17. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology Ltd., London, p. 57 (1998).
18. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology Ltd., London, p. 59 (1998).
19. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology Ltd., London, p. 63 (1998).
20. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology Ltd., London, p. 65 (1998).

21. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology Ltd., London, p. 71 (1998).

22. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology Ltd., London, p. 72 (1998).

23. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology Ltd., London, p. 67 (1998).

24. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology Ltd., London, p. 68 (1998).

25. Beying, A., *RadTech Europe '97, Conference Proceedings* (June 16–18, Lyon, France), p. 77 (1997).

26. Läuppi, U. V., *RadTech Europe '97, Conference Proceedings* (June 16–18, Lyon, France), p. 96 (1997).

27. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV & EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology, London, p. 141 (1998).

28. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV & EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology, London, p. 143 (1998).

29. Bradley, R., *Radiation Technology Handbook*, Marcel Dekker, New York, 1984, p. 37 (1983).

30. Chrusciel, J., private communication.

31. Artandi, C., and Van Winkle Jr., W., *Nucleonics*, 17, p. 86 (1959).

32. Charlton, E. E., Westendorp, W. F., and Dempster, L. E., *J. Appl. Phys.*, 10, p. 374 (1939).

33. Cleland, M. R., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, Chapter 3, p. 28 (1992).

34. Sakamoto, I., Mizusawa, K., *Radiat. Phys. Chem.*, 18, p. 1341 (1981).

35. Scharf, W., *Particle Accelerators and Their Uses*, Harwood Academic Publishers, New York (1986).

36. Abramyan, E. A., *Industrial Electron Accelerators and Applications*, Hemisphere, Washington, DC (1988).

37. Van de Graaff, R. J., U.S. Patents 3,187,208 (1965), 3,289,066 (1966), 3,323,069 (1967).

38. Emanuelson, R., Fernald, R., and Schmidt, C., *Radiat. Phys. Chem.*, 14, p. 343 (1979).

39. Sakamoto, I. et al., *Radiat. Phys. Chem.*, 25, p. 911 (1985).

40. Cleland, M. R., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, Chapter 3, p. 29 (1992).

41. Cleland, M. R., Thompson, C. C., and Malone, H. F., *Radiat. Phys. Chem.*, 9, p. 547 (1977).

42. Thompson, C. C., and Cleland, M. R., *Nucl. Instrum. Meth.*, B40/41, p. 1137 (1989).

43. Morganstern, K. H., *Proceedings of the Conference on Sterilization of Medical Products*, Vol. 4, Johnson & Johnson, Polyscience Publications, Montreal (1986).

44. Odera, M., Nagakura, K., and Tanaka, Y., *Radiat. Phys. Chem.*, 35, p. 534 (1990).

45. Cleland, M. R., Thompson, C. C., Strelczyk, M., and Sloan, D. P., *Radiat. Phys. Chem.*, 35, p. 632 (1990).

46. Cleland, M. R., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, Chapter 3, p. 29 (1992).

47. Cleland, M. R., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, Chapter 3, p. 30 (1992).

48. Haimson, J., *Proceedings of the Conference on Sterilization by Ionizing Radiation 1*, Johnson & Johnson, Multiscience Publications Ltd., Montreal (1974).

49. Haimson, J., *IEEE Trans. Nucl. Sci.*, NS-22, p. 1303 (1975).

50. Cleland, M. R., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, Chapter 3, p. 30 (1992).

51. Anonymous, *Beta-Gamma*, 3, p. 38 (1989).

52. Auslender, V. L., et al., U.S. Patent 4,140,942 (1979).

53. Cleland, M. R., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, Chapter 3, p. 34 (1992).

54. Barletta, W. A., *Beam Research Program, Energy and Technology Review*, Lawrence Livermore National Laboratory, Livermore, LLL TB 63 (1984).

55. Humphries Jr., S., *Principles of Charged Particles Acceleration*, John Wiley & Sons, New York (1986).

56. Lapostolle, P. M., and Septier, A. L., *Linear Accelerators*, North Holland Publishers, Amsterdam (1970).

57. Abs, M., Jongen, Y., Poncelet, E., and Bol, J.-L., *Radiat. Phys. Chem.*, 71, p. 285 (2004).

58. Lancker, M. V., Herer, A., Cleland, M. R., Jongen, Y., and Abs, M., *Nucl. Instrum. Meth.*, B151, p. 242 (1999).

59. Jongen, Y., Abs, M., Genin, F., Nguyen, A., Capdevilla, J. M., and Defrise, D., *Nucl. Instrum. Meth.*, B79, p. 8650 (1993).

60. Korenev, S., *Radiat. Phys. Chem.*, 71, p. 535 (2004).

61. Korenev, S., *Radiat. Phys. Chem.*, 71, p. 277 (2009).

62. Meissner, J., Abs, M., Cleland, M. R., Herer, A. S., Jongen, Y., Kuntz, F., and Strasser, A., *Radiat. Phys. Chem.*, 57, p. 647 (2000).

63. Bassaler, J. M., Capdevilla, J. M., Gal, D., Lainé, F., Nguyen, A., Nicolai, J. P., and Uniastowski, K., *Nucl. Instrum. Meth.*, B68, Issue 1-4, p. 92 (1992).

64. Singh, A., and Silverman, J., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, Chapter 1, p. 10 (1992).

65. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV & EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology, London, p. 139 (1998).

66. Holl, P., *Radiation Physics and Chemistry*, 25, p. 665 (1985).

67. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV & EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology, London, p. 150 (1998).

68. Meskan, D. A., and Klein, F. A., *Proceedings, RadTech Europe '97* (June 16–18, Lyon France), p. 114 (1997).

69. Schwab, U., *Proceedings RadTech Europe '97* (June 16–18, Lyon, France), p. 114 (1997).

70. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV & EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology, London, p. 155 (1998).

71. Chrusciel, J., private communication.

72. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV & EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology, London, p. 156 (1998).

73. Maguire, E. F., *RadTech Report*, 12, No. 5, September/October, p. 18 (1998).
74. Davis, J. I., and Wakalopulos, G., *Proceedings RadTech North America '96*, p. 317 (1996).
75. Wakalopulos, G., *RadTech Report*, 12, No. 4, July/August, p. 18 (1998).
76. Brochure, Advanced Electron Beams, Wilmington, MA.
77. Berejka, A. J., et al., *Proceedings RadTech North America 2009* (April 28–May 1, Indianapolis, IN), p. 919 (2002).
78. Avnery, T., U.S. Patents 5,962,995 (1999) and 6,545,398 (2003) to advanced electron beams.
79. Berejka, A. J., *Radiat. Phys. Chem.*, 71, p. 309 (2004).

# 4

## UV Radiation Processes

Electromagnetic radiation (or light) can be used as the energy source for a variety of processes involving functional monomers, oligomers, and polymers. In these processes, it is utilized mainly to effect the formation of new chemical bonds. The light used in polymeric systems typically has wavelengths ranging in the ultraviolet spectral range extending from 200 to 400 nm, although in some special cases it may include wavelength in the visible range up to 760 nm. Xenon lamps provide significant emissions in the 450 to 550 nm range.[1] Since the energy of radiation increases with increasing frequency (or decreasing wavelength), radiation with short waves contains a large amount of energy. This energy is capable of bringing about certain chemical reactions in a system that is sensitive to light, which means that it has the ability to absorb it. Then the absorbed energy can generate species, which are capable of initiating polymerization or cross-linking reactions.

For the most part, UV radiation is used to convert reactive liquid monomers and oligomers to solids. This process involves essentially polymerization and sometimes polymerization and cross-linking simultaneously. Monomers and oligomers with a functionality of two form linear polymers, whereas multifunctional ones (with a functionality of more than two) yield three-dimensional cross-linked networks. Cross-linking imparts solvent resistance, increases hardness, and improves heat resistance. The main practical utility of these reactions is in curing coatings and inks and in photoimaging. Cross-linking of already existing polymers is also a viable process and is currently a very active field of research.[1]

## 4.1 Basic Concepts

The processes of photochemistry are the same for polymers and small molecules.[2–6] The *Grotthus-Draper law* states that no photochemical reactions can occur unless a photon of light is absorbed. This means, for example, that many commercial plastics transparent in the near UV can undergo photodegradation only as a result of the absorption of light by impurities.

The intensity of any light absorbed by a light-absorbing species (chromophores) follows Lambert-Beer's law:

$$I = I_0 \, 10^{-\varepsilon c d}$$
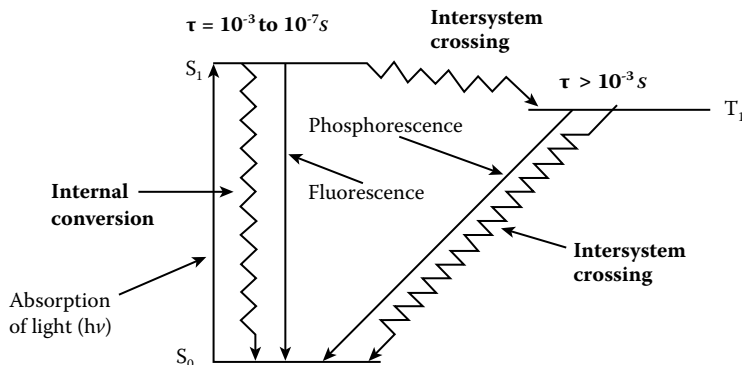
**FIGURE 4.1**
Primary processes occurring in the excited state of a UV radical photoinitiator. (Adapted from Jablonski, A., *Z. Physik*, 94, p. 38 (1935).)

where $I_0$ is the intensity of the incident light, I is the intensity of transmitted light, $\varepsilon$ is the molar extinction coefficient ($cm^{-1}$ $mol^{-1}$), c is concentration of absorbing species, and d is the optical path length.

*Absorbance* (A), or optical density, is defined as $-\log (I/I_0)$; then $A = \varepsilon cd$.

Typical chromophoric groups for UV light are $-C=O$, $-ROOH$, and aromatic groups. These extend the absorption of monomers, oligomers, and polymers into the UV light range.[7] Figure 4.1 shows an energy level (Jablonski) diagram for a ketone, a common chromophore in polymers.[8] Several intramolecular processes are shown competing with photochemical reactions, including reemission of a photon as fluorescence or phosphorescence, radiationless decay to the ground state, and crossing from one excited state to another.

The ground states of almost all organic compounds have all electron spins paired. Absorption of a photon promotes an electron from the singlet state, $S_0$, to a higher-energy singlet state, $S_1, S_2, ..., S_n$, numbered in the order of increasing energy above the ground state. A change in the spin state of an electronically excited molecule is called *intersystem crossing*; it produces triplet species, $T_1, T_2, ..., T_n$, with two unpaired spins.[9] A triplet state is always lower in energy than the corresponding singlet state. Singlet and triplet states may emit light and return to the ground state.[10]

To put it simply:

- The absorption of a photon by a chromophore brings about a transition into the excited singlet state.
- Generally, the excited molecule has two possibilities to emit the absorbed energy: it can either return to the ground state by emitting energy by fluorescence or a nonradiative transition, or can cross over to the excited triplet state.[10]

- Molecules in the triplet state are biradicals, which can, if the energy is high enough for breaking a bond, form free radicals. The free radicals can then initiate the polymerization or cross-linking reaction.

The main decay processes to the ground state shown in Figure 4.1, which is essentially an energy diagram for the different electronic states, are:

- Radiative processes:
  - Absorption: $S_0 + h\nu \rightarrow S_1$
  - Fluorescence: $S_1 \rightarrow S_0 + h\nu'$
- Phosphorescence: $T_1 \rightarrow S_0 + h\nu''$

  where h is the Planck's constant and $\nu$, $\nu'$, and $\nu''$ are the respective frequencies of the absorbed or emitted light.

- Radiationless processes:
  - Internal conversion: $S_1 \rightarrow S_0 + heat$
- Intersystem crossing: $T_1 \rightarrow S_0$ or $S_1 \rightarrow T_1$

The result of a photochemical reaction involving monomers, oligomers, and polymers depends on the chemical nature of the material, wavelength of the light, and other components of the system. Ultraviolet, visible, and laser light can polymerize functional monomers, cross-link polymers,[1] or degrade them, particularly in the presence of oxygen.[11]

---

## 4.2 Photoinitiators and Photosensitizers

There are essentially two types of compounds that are used in the UV curing process to absorb the light and generate reactive species. These are photoinitiators and photosensitizers.

*Photoinitiator* (PI) is a compound generating reactive species that will initiate polymerization or cross-linking. *Photosensitizer* (S) is a compound that will energize certain species that will in turn lead to production of reactive species. It is a molecule that absorbs light usually at longer wavelengths and transfers energy to a photoinitiator to generate free radicals or ions.

$$PI \rightarrow PI^* \rightarrow \text{Reactive species (free radicals or ions), or } S \rightarrow S^*$$

$$S^* + PI \rightarrow S + PI^* \qquad \text{Energy transfer to photoinitiator}$$
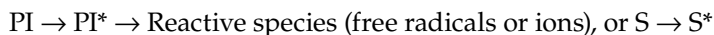
Thus, photosensitizers are useful mainly by being capable of extending the spectral sensitivity of certain photoinitiators under specific conditions.

The function of a photoinitiator is:

- Absorbing the incident UV radiation
- Generating reactive species (free radicals or ions)
- Initiating photopolymerization

In the UV curing process, photons from the UV source are absorbed by a chromophoric site of a molecule in a single event. The chromophore is a part of the photoinitiator. The light absorption by the photoinitiator requires that an emission light from the light source overlap with an absorption band of the photoinitiator.

The photon absorption follows Lambert-Beer's law (see above). The number of photons I present at depth l from the surface is given as a function of the optical absorbance, A, normalized to the initial number of photons, $I_0$:

$$\log (I_0/I) = A = \varepsilon \, [PI] \, l$$

where [PI] is the concentration of photoinitiator. The quantity l is also termed the *photon penetration path.*

In general, upon exposure to UV radiant energy, a photoinitiator can generate free radicals or ions, as pointed out earlier. These are generated at a rapid rate, and their depth profile corresponds to the inverse photon penetration profile. Similar to electron penetration, the final cure profile often deviates from the initial radical or ion distribution, since they can live much longer than the exposure time. The mechanisms of the processes for the generation of reactive species are discussed in detail in Davidson.[12]

Depending on the type of reactive species generated upon exposure to UV light, photoinitiators are classified as free radical, cationic, and anionic.

## 4.2.1 Free Radical Photoinitiators

The UV curing of certain monomers, such as acrylate, methacrylate, and maleate/vinyl ether systems, is initiated by free radicals. In all practical cases, the initiating radicals are generated from electronically excited photoinitiator molecules.[13,14] A photoinitiator molecule is excited into the singlet state by the absorption of a photon. The formation of a radical occurs via a triplet state. Radical formation occurs via two possible reaction sequences. They are designated as Norrish type I and type II reactions. In a type I reaction the photoinitiator triplet state decays into a radical pair by homolytic decomposition and directly forms radicals capable of initiating polymerization. The absorbed radiation causes bond breakage to take place between a carbonyl group and an adjacent carbon. In type II Norrish reaction, triplet states of ketones possessing an α-hydrogen preferably react with suitable hydrogen-donating compounds by hydrogen abstraction. The resulting radical pair can be generated either by a homolytic cleavage of the R–H bond or via an intermediate charge transfer complex followed by proton transfer.[15] The lifetime of the excited initiator species is very short, generally less than $10^{-6}$ s. During this time it may be partitioned essentially between two processes: it can decay back to the original state with emission of light or heat or yield a reactive intermediate (free radical or ion), which in turn can react with another free radical or initiate polymerization of a monomer.[16]

Free-radical photoinitiators are classified by their chemical nature as type I and type II; however, there are a few systems with different chemistry, e.g., borate salt initiators that depend on inter-/intramolecular electron transfer,[17] that do not fit into either category.

### 4.2.1.1 Type I Photoinitiators

Type I initiators are compounds that upon irradiation undergo a cleavage reaction (α- or β-cleavage) to generate two radicals:[18]
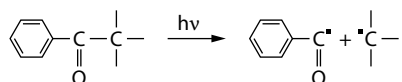


The chromophore in this type of photoinitiator is frequently an aromatic carbonyl. The benzoyl radical is the major initiating species, while the other fragment may also contribute to the initiation, in some cases. The most efficient type I initiators are benzoin ether derivatives, benzil ketals, hydroxyl-alkylphenones, α-aminoketones, and acylphosphine oxides.[19] Substituents on the aromatic carbonyl influence the absorption.

### 4 2.1.2 Type II Photoinitiators

A large number of aromatic ketones (benzophenone, substituted benzophenone, benzil, fluorenone, camphorquinone, xanthone, and thioxantone)[10] will act as type II initiators, with their performance being dramatically enhanced by the use of tertiary amine synergists. There are essentially two classes of amine synergists, aliphatic and aromatic, with different characteristics and uses.[20] Aliphatic amines are transparent down to about 260 nm, and consequently, a coating containing such amine can be cured with UV light down to that wavelength. Aromatic amine synergists display strong absorption around 300 nm and consequently screen much of the UV light.[21] Therefore, in cures with benzophenone it is best to use an aliphatic amine, whereas thioxanthones, because of their strong absorption at wavelengths greater than 340 nm, can be used successfully with an aromatic amine.[20]

Combinations of type I and type II photoinitiators are used to reduce air inhibition in the absence of amines.[22] A possible explanation of the synergistic effect is that the photocleavage of the type I initiator yields free radicals that react with oxygen to generate peroxy-radicals (R-O-O•). These radicals are poor initiators for usual radical polymerization, but they abstract hydrogen from monomers and oligomers, which regenerates radicals (chain process). Oxygen depletion enhances the effectiveness of type II initiators as an energy transfer agent for decomposing hydroperoxides into alkoxy (RO•) and hydroxy (HO•) radicals.[23] In contrast to peroxy radicals, they are highly effective initiators for acrylate polymerization. In the overall process, oxygen is used to produce initiating radicals.

Some examples of type I and type II photoinitiators are shown in Tables 4.1 and 4.2, respectively.

## 4.2.2 Cationic Photoinitiators

Cationic photoinitiators are compounds that, under the influence of UV or visible radiation, release an acid, which in turn catalyzes the desired polymerization process.[24] Initially, diazonium salts were used, but they were replaced by more thermally stable iodonium and sulfonium salts.[25] Examples of cationic initiators are in Table 4.3.

## 4.2.3 Anionic Photoinitiators

Tertiary amine salts of ketocarboxylic acids[26] were used initially. Newer systems based on peptide chemistry have been described and used in microlithography.[27]

## 4.2.4 Oxygen Inhibition of Cure

Oxygen decreases the efficiency of radical curing processes by quenching the triplet states of photoinitiators, scavenging radicals generated by the initiator system, and scavenging the growing macroradical.[28] In thin films, oxygen inhibition manifests itself by surface tack of cured films. To prevent this, the curing can be carried out under nitrogen blanket or by covering the film by a protective layer, such as thin sheet of polyester. Another method is to incorporate a tertiary amine into the system. The latter method is preferred for UV curing[29]; however, it has a drawback, namely, an increased rate of photo-yellowing of cured films.[30]

## 4.2.5 Initiation of UV Hybrid Curing

Certain UV curing systems undergo polymerization by two different mechanisms, which is referred to as hybrid curing.[31] Photodecomposition of arylsulfonium salts generates both radicals and Brønsted acids. For example, the formed radicals can initiate the polymerization of acrylates, and the acid initiates the polymerization of vinyl ethers. In acrylate systems containing a cationic photoinitiator, the acrylate polymerization is greatly accelerated by the addition of vinyl ethers. On the other hand, the vinyl ether component is cured cationically. This produces interpenetrating polymer networks, containing both the acrylate and vinyl ether component. Vinyl ethers as good hydrogen donors enhance photoinduced radical production from aryl sulfonium initiators, thus increasing the initiation rate of acrylate polymerization.[32]

In comparison with cationic curing systems, hybrid curing systems increase the rate of cure, produce cured films with improved solvent resistance, and offer a greater formulation latitude. When compared to free radical cure, better

**TABLE 4.1**

Examples of Type I Photoinitiators

R$_1$= H$_3$CS,

R$_2$= CH$_3$, CH$_2$Ph , C$_2$H$_5$

R$_3$= N(CH$_3$)$_3$,

Aminoalkylphenones

R$_1$= H or alkyl

R$_2$= H or substituted alkyl

Benzoin ethers

R$_1$=H, iso-C$_3$H$_7$, HOCH$_2$CH$_2$O

R$_2$ = CH$_3$, OCH$_3$, OC$_2$H$_5$

R$_3$ = H, Ph, OH

Acetophenones

R = C$_6$H$_5$ , OCH$_3$
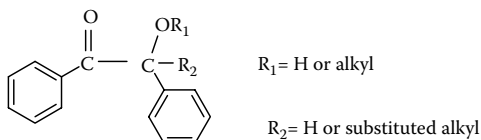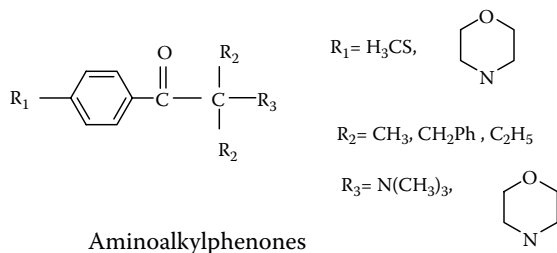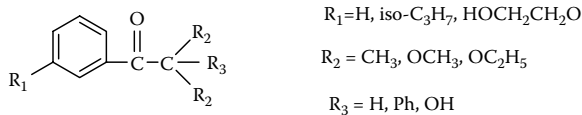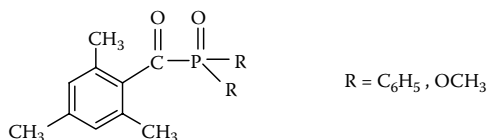
Acylphosphines
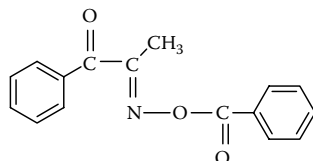
Benzoyloximes

**TABLE 4.2**

Examples of Type II Photoinitiators
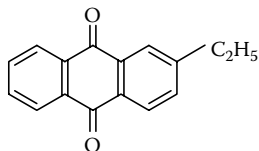
Anthrachinones
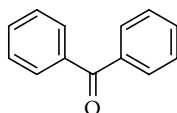
Benzophenone
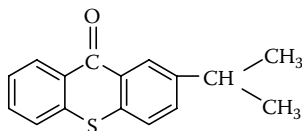
2-Isopropyl thioxanthone (ITX)

adhesion to critical substrates and lower oxygen sensitivity are observed in some cases.[33]
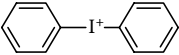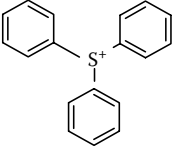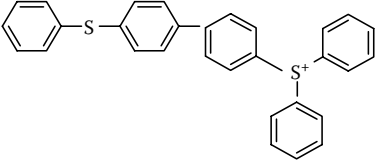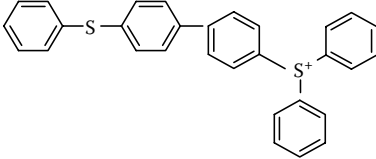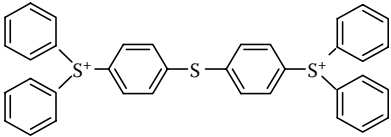
## 4.3  Kinetics of Photoinitiated Reactions

### 4.3.1  Kinetics of Free Radical Photopolymerization

Photoinitiated free radical polymerization proceeds via three main steps:

1. Initiation
2. Chain propagation
3. Termination

**TABLE 4.3**

Examples of Cationic Photoinitiators



The initiation rate, $v_i$, depends on the radical yield per absorbed photon, $\Phi_i$, and the number of photons absorbed per second in a unit volume, $I_a$. The latter quantity is a fraction of $I_0$, the number of photons per second per unit volume entering the process zone.

Initiation step:  AB* $\rightarrow$ $\bullet R_1 + \bullet R_2$ ($\bullet R_1$, $\bullet R_2$ – free radicals)

$\bullet R_1$, $\bullet R_2 + M \rightarrow \bullet P_1$
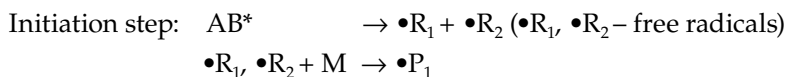
Initiation rate:  $v_i = \Phi_i\, I_a$

In the chain propagation, mainly the monomer is consumed and the propagation rate depends on the monomer concentration, [M], and the concentration of polymeric radicals, [$\bullet P_n$]. The quantity $k_p$ is the propagation rate constant.

Propagation step:       $\bullet P_n + M \rightarrow \bullet P_{n+1}$
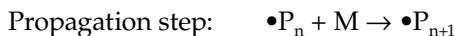
Propagation rate:       $v_p = k_p [\bullet P_n] [M]$

Chain termination occurs by combination or disproportionation of different polymer radicals. The termination rate, $v_t$, is proportional to the polymer radical concentration, [$\bullet P_n$], squared, with $k_t$ being the termination rate constant. Other possible chain termination processes are chain transfer and reaction of polymer radicals with inhibitors and radical trapping.[34]

Termination step:       $\bullet P_n + \bullet P_m \rightarrow P_n - P_m$

or $P'_n - P_m$ (chain transfer)
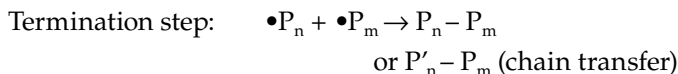
Termination rate:       $v_t = k_t [\bullet P_n]^2$

Since $v_i = v_t$, then

$$v_p = k_p/(k_t)^{-\frac{1}{2}}[M] (\Phi_i I_a)^{\frac{1}{2}}$$

and thus

$$v_p \sim I_0 (1 - \exp(-2.303 \, \varepsilon \, [PI] \, l))^{\frac{1}{2}}$$

The assumptions made to estimate the propagation rate, $v_p$, which is essentially the rate of the polymerization reaction, are:

1. The light used is monochromatic and is absorbed by the photoinitiator exclusively.
2. The absorption is small and homogeneous within the irradiated volume.
3. As the polymerization proceeds, a stationary radical concentration is obtained.
4. All polymer radicals exhibit the same reactivity toward propagation and termination.

### 4.3.2   Kinetics of Cationic Photopolymerization

Cationic polymerization is initiated either by strong Lewis acids such as $BF_3$ or $PF_5$ or by Brønsted acids such as $H^+BF_4$, $H^+PF_6$, or $H^+SbF_6$. Lewis acids are generated by UV irradiation of aryldiazonium salts, whereas diaryliodonium, triarylsulfonium, and triarylselenium salts produce upon UV

irradiation strong Brønsted acids. The latter are preferred as initiating species in cationic polymerization.[35]

Reaction steps in a photoinduced cationic polymerization are as follows:

| | | | |
|---|---|---|---|
| Initiation: | $H^+X^- + M$ | $\rightarrow$ | $H-M^+ + X^-$ |
| Propagation: | $H-M^+ + nM$ | $\rightarrow$ | $H-(M)_nM^+$ |
| Chain transfer: | $H-(M)_nM^+ + ROH$ | $\rightarrow$ | $H-(M)_nM-OR + H^+$ |
| Termination: | $H-(M)_nM^+ + A^-$ | $\rightarrow$ | $H-(M)_nMA$ |
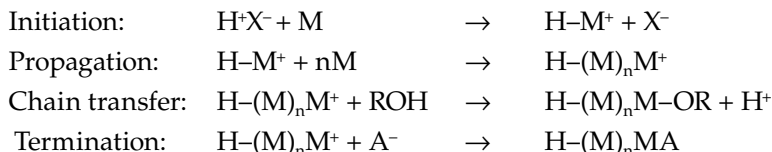
In the initiation step, the monomer, M, is initiated by intermediate protonation followed by the formation of a carbocation, $H-M^+$. Propagation can be terminated by anionic or nucleophilic species, $A^-$. If a hydroxy-functional compound (ROH) is present, chain transfer can occur via proton formation.

Photochemical decomposition of cationic photoinitiators can be sensitized by energy or electron transfer from the excited state of a sensitizer. Certain sensitizers, such as isopropylthioxantone, anthracene, or even certain dyes absorbing in the visible region, can be used to shift excitation to higher wavelengths. In such cases, visible light, for example, from tungsten lamps, can be used for photocuring.

There are several differences between the photoinitiated cationic polymerization and the photoinduced free radical polymerization:

1. The initiating species is a stable compound consumed only by anions and nucleophiles.
2. After the exposure to UV light, cationic polymerization continues for a long time.
3. Cationic systems are sensitive to humidity.
4. Cationic polymerization is not affected by oxygen the way the free radical polymerization is.
5. Cationic systems are generally slower than free radical curing systems.

A comprehensive review of the kinetics of photopolymerization of multifunctional monomers was published by Andrzejewska.[36]

## 4.4 Chemical Systems in UV Processing

The essential ingredients of any system processed by UV are:

- A reactive base oligomer, which imparts most of the properties to the final cured or cross-linked material; the molecular weight of oligomers used in UV processing is typically in the range from 400 to 7,000.

- Monofunctional monomer (or monomers) used to dilute the formulation to the suitable application viscosity.
- Multifunctional monomer(s) creating cross-links between segments of the oligomer and also acting as reactive diluent(s).[34]

There are many possibilities, but only a few systems are being used for practical UV curable formulations using free radical or cationic initiation. These will be discussed in this section.

### 4.4.1  Free-Radical-Initiated Systems

#### 4.4.1.1  Acrylate/Methacrylate Systems

The most widely used UV curable radical-initiated systems are based on acrylate unsaturation with the general formula $H_2C = CR–COOR'$ (if R = H, the monomer is an acrylatel; if R = $CH_3$, it is a methacrylate). Methacrylates are less reactive than acrylates,[37] but are less toxic and cause less skin irritation than acrylates.

The curing reaction of acrylates is typical of vinyl monomers. Therefore, the degree of double-bond conversion is the measure of the degree of cure.[38] The best results are obtained when using oligomers as binders and monomers as reactive thinners. Examples of difunctional and polyfunctional acrylates are in Table 4.4. A partial list of the most common acrylate oligomers is below.[14,39,40]

*Epoxy acrylates*: The most widely used oligomers are aromatic and aliphatic epoxy acrylates. Epoxy acrylates are highly reactive and produce hard and chemically resistant films. The polymerization of monoacrylates produces linear polymers, whereas diacrylates produce branching and higher-functionality acrylates give rise to cross-linked structures. Cured materials are useful as coatings and adhesives on rigid substrates, such as metal cans and paneling, or as binders in composites. The epoxy component contributes to adhesion to nonporous substrates and enhances chemical resistance of the film.

*Urethane acrylates*: Urethane acrylates are formed by the reaction of isocyanates with hydroxy-functional acrylate monomers. After UV cure, they produce tough, flexible materials, which exhibit a good abrasion resistance.

*Polyester acrylates*: Acrylated polyesters are prepared by reacting the OH group of polyesters with acrylic acid or hydroxy acrylate with acid groups of the polyester structure. Polyester acrylates are often low-viscosity resins requiring little or no monomer.[41] They produce coatings and adhesives dominated by the polyester structure used in the oligomer. They are used for pressure-sensitive adhesives and

**TABLE 4.4**

Examples of Difunctional and Polyfunctional Acrylates Used in UV Curing

| Monomer | Type of Main Chain | Functionality | Abbreviation | Molecular Weight | Viscosity, mPa.s at 25°C |
|---|---|---|---|---|---|
| 1,6-Hexanediol diacrylate | Linear hydrocarbon | 2 | HDDA | 226 | 5–10 |
| Tripropyleneglycol diacrylate | Branched ether | 2 | TPGDA | 300 | 10–20 |
| Dipropyleneglycol diacrylate | Branched ether | 2 | DPGDA | 242 | 8–12 |
| Trimethylolpropane triacrylate | Branched hydrocarbon | 3 | TMPTA | 296 | 50–150 |
| Pentaerythritol triacrylate | Branched hydrocarbon | 3 | PETA | 298 | 350–700 |
| Ditrimethylolpropane tetraacrylate | Branched ether | 4 | DTMPTA | 438 | 450–900 |
| Dipentaerythritol pentaacrylate | Branched ether | 5 | DPEPA | 525 | 14,000 |

also for strong rigid adhesives for metal-to-metal bonding. Amino-
modified polyester acrylates show a high reactivity and low skin
irritation.

*Silicone acrylates*: Acrylated organopolysiloxanes exhibit excellent
release properties and are used as release coatings on papers and
films. The silicone structure provides flexibility and resistance to
heat, moisture, radiation degradation, and shear forces.[41]

*Polyether acrylates*: Polyether acrylates are produced by esterification of
polyetherols with acrylic acid. They have a very low viscosity and do
not require reactive thinners. Amino-modified polyether acrylates
have a higher reactivity and low skin irritance, similar to polyester
acrylates.

Solid urethane and polyester acrylates may be used as main components
of radiation curable powders. Together with suitable unsaturated polyesters,
powders are formed, which give low-film-flow temperatures and allow sepa-
rating of film formation from curing. This technology has been used success-
fully in powder coating of wood and plastics.[42]

### 4.4.1.2  Styrene/Unsaturated Polyesters

Unsaturated polyesters have been among the earliest commercially avail-
able radiation curable systems. They are condensation products of organic
diacids (or anhydrides) and glycols, most frequently using phtallic or maleic
anhydride and 1,2 propylene glycol. In commercial systems, styrene is used
as reactive diluent (at 20 to 40 wt.%) for unsaturated esters prepared from
maleic anhydride and fumaric acid. The polymerization of styrene can be
initiated by a wide range of thermal and type I photoinitiators. Type II ini-
tiators cannot always be used because styrene quenches the triplet state of
many carbonyl compounds.[43] The resulting product is styrene-polyester
copolymer. The styrene/unsaturated polyester system is relatively slow but
inexpensive, and therefore has been used extensively for wood coatings, yet
there is a tendency to replace them by acrylates.[44]

### 4.4.1.3  Vinyl Ether/Unsaturated Esters

When using a suitable type I photoinitiator, e.g., acylphosphine oxides
and non-amine-containing acetophenones in this system, the polymeriza-
tion process is very efficient and the resulting product is a 1:1 alternat-
ing copolymer.[45] This system is susceptible to oxygen inhibition, but to a
much lesser extent than acrylate polymerization.[46] An important advan-
tage of this system is its low toxicity. Typical components include a variety
of vinyl ethers and unsaturated esters, such as maleate, fumarate, citra-
conate, imides (maleimides), or N-vinylformamides.[47] The system is also

referred to as a maleate/vinyl ether (MA/VE) system since maleates are widely used in commercial products. The most widely commercially used are systems consisting of oligomer components, which are not skin irritating or sensitizing and exhibit a low vapor pressure. However, their cure speed is lower than that of acrylates. When radicals are generated by conventional photoinitiators, copolymerization occurs via an *electron donor-acceptor complex* (see Section 4.4.1.5). For practical applications, oligomeric MA/VA systems have been developed, consisting of maleate end caps and polyester, epoxy, or urethane backbone section, which is diluted by means of a vinyl ether.[48]

### 4.4.1.4  Thiol-ene Systems

This reaction is based on a stoichiometric reaction of multifunctional olefins (*enes*) with *thiols.* The addition reaction can be initiated thermally, photochemically, and by electron beam and radical or ionic mechanism.[49] Thiyl radicals can be generated by the reaction of an excited carbonyl compound (usually in its triplet state) with a thiol or via radicals, such as benzoyl radicals from a type I photoinitiator, reacting with the thiol. The thiyl radicals add to olefins, and this is the basis of the polymerization process.[50] The addition of a dithiol to a diolefin yields linear polymer, higher-functionality thiols and alkenes form cross-linked systems.

The most important attribute of the thiol-ene system is its insensitivity to oxygen; thus, it is not inhibited by it. Another attractive feature is its very high cure speed. The disadvantage of the thiol-ene system is an unpleasant odor of the volatiles emitted from some polythiol compounds.[47,51]

### 4.4.1.5  Donor-Acceptor Complexes

Another method to generate an initiating radical pair is by using donor-acceptor complexes (DACs). Unsaturated molecules containing an excess electron charge at the double bond, such as vinyl ethers or styryloxy derivatives mixed with molecules that have electron-deficient unsaturation, such as maleic anhydride, maleates, or fumarates, form either *ground state* DAC (during mixing) or *excited state* DAC (after irradiation). Examples of such pairs are below:[52]

> Methoxy styrene (donor)–maleic anhydride (acceptor)
>
> Triethylene glycol divinyl ether (donor)–maleimide (acceptor)
>
> 1,4-Cyclohexane dimethanol divinyl ether (donor)–alkyl maleimide (acceptor)

The excited donor-acceptor complex undergoes hydrogen abstraction or electron transfer, thus generating the initiating radical pair for subsequent

copolymerization. Some electron acceptors form strong chromophores for UV absorption, thus having the same function as a conventional photoinitiator, by being the source of free radicals. Such systems are potentially UV nonacrylate curing systems without photoinitiators.

Another development is free radical polymerization of neat acrylates without photoinitiator using 172 and 222 nm excimer lamps. Photons emitted from these radiation sources are absorbed by many acrylates generating free radicals directly.[53]

The development of self-curing resins, i.e., systems curing without photoinitiators or, in some cases, with just small amounts of photoinitiators, has been reported recently.[54] Such resins are synthesized by Michael reaction of acrylic functional materials with Michael donor compounds such as acetoacetates. The resulting product has an increased molecular weight compared to the parent acrylate(s). This provides resins with reduced volatility and propensity for skin absorption. This new technology is versatile and flexible and opens a possibility of synthesis of a large number of different acrylate resins. The novel resins reportedly exhibit unique depth of cure capability. In the absence of a photoinitiator (PI), film of approximately 10 mils (0.25 mm) thick can be cured at a line speed of 100 fpm (30.5 m/min). When only 1% of PI is added, the thickness of film that can be cured increases to over 100 mils (2.5 mm).

### 4.4.2 Cationic Systems

As pointed out in Section 4.2.2, cationic polymerization processes are initiated by photoinitiators, which are essentially precursors generating Lewis and Brønsted acids. The mechanism of the process is ionic, and this chemistry does not function with the type of double bonds and unsaturation found in the monomers and oligomers reacting via free radical mechanism.

Cationic photoinitiation is based on the ring opening of the oxirane group. The photoinitiators of practical importance belong to three main classes of compounds: diazonium salts, onium (e.g., iodonium and sulfonium) salts, and organometallic complexes,[55] which upon irradiation by UV light decompose and yield an acid catalyst.

Aliphatic and cycloaliphatic epoxides (oxiranes) are by far the most frequently used substances in cationic process. However, cationic curing is not restricted to epoxies. Vinyl esters can also polymerize by a cationic mechanism and form an interpenetrating polymeric network when blended with epoxies. Multifunctional polyols are frequently used in cationic UV curing formulations as chain transfer agents, improving the cure speed, modifying the cross-link density, and affecting the flexibility of the coating.[56]

Epoxy-functional polydimethylsiloxane oligomers are another group that can be cured by UV radiation. Epoxysilicone block copolymers exhibit a good photoinitiator miscibility, high cure rate, and compatibility with epoxy and vinyl ether monomers. These block copolymers form flexible films with excellent release properties and are therefore used as release coatings.[57]

**TABLE 4.5**

Example of a General-Purpose Cationic UV Curable Formulation

| Ingredient | Function | Weight % |
|---|---|---|
| Cycloaliphatic epoxide resin[a] | Base resin | 70.4 |
| ε-Caprolactone triol | Flexibilizer and cross-linker | 25.1 |
| Arylsulfonium salts[b] | Photoinitiator | 4.0 |
| Silwet L-7604[c3] | Silicone surfactant | 0.5 |
| Total | | 100.0 |

*Source:* Cyracure Cycloaliphatic Epoxies, Cationic UV Cure, Form 321-00013-0901 AMS, Dow Chemical Company (2001).

[a] 3,4-Epoxycyclohexylmethyl-3,4 epoxycyclohexane carboxylate.
[b] Mixed arylsulfonium hexafluorophosphate salts.
[c] OSi Specialities.

Cationically cured coatings exhibit a good adhesion to varied substrates, impact resistance, chemical resistance, and high hardness and abrasion resistance. The cure speed of cationic systems is generally lower than that of acrylates. Cationic cure is not affected by oxygen, but it is negatively affected by ambient humidity, amines, or other bases, and even by certain pigments. Heat increases the cure speed and often the ultimate degree of conversion. The acids generated by UV irradiation continue to be active even after the exposure stops. A pronounced dark postcure effect is observed and may last several days.[57] An example of a general purpose cationic formulation is in Table 4.5.

## 4.5 Photo-Cross-Linking of Polymers

While photopolymerization and photo-cross-linking of oligomers (or low-molecular-weight polymers) and monomers are well established in industrial practice and widely used, a great deal of research has been conducted on the photo-cross-linking of high-molecular-weight polymers.[58] The energy sources for this process are high-intensity UV and visible light and lasers (1–10$^2$ eV), particularly in industrial applications.[59–61] The photoinitiators may be added to the polymer or grafted onto the polymer chains. Photocycloaddition involving poly(vinyl cinnamate), chalcone types of compounds, bismaleimides, antracene derivatives, cyclized polyisoprene,[62–64] and formation of cyclobutane ring by dimerization[65] and thiol-ene reactions based on polythiol and polyene (a polyunsaturated co-reactant) (see Section 4.4.1.4) using an aromatic ketone as photoinitiator[66] are examples of photo-cross-linking.

Since many polymers are to a certain degree photo-cross-linkable and photodegradable, the result of the overall reaction depends on the prevailing process, because cross-linking and degradation are competing processes.

The photo-cross-linkability of a polymer depends not only on its chemical structure, but also on its molecular weight and the ordering of the polymer segments. Vinyl polymers, such as PE, PP, polystyrene, polyacrylates, and PVC, predominantly cross-link, whereas vinylidene polymers (polyisobutylene, poly-2-methylstyrene, polymethacrylates, and polyvinylidene chloride) tend to degrade. Likewise, polymers formed from diene monomers and linear condensation products, such as polyesters and polyamides, cross-link easily, whereas cellulose and cellulose derivatives degrade easily.[67]

There are several interesting applications reported in the literature, such as insulated wire and cable,[68,69] UV cross-linking of drawn fibers, and tapes from ultra-high-molecular-weight polyethylene.[70–72] Semi-interpenetrating networks (IPNs) from acrylates and polyurethanes are suitable as UV curable adhesives with high elasticity, good impact resistance, and excellent adhesion to a variety of substrates.[73,74]

The subject of photo-cross-linking is reviewed thoroughly by Rånby et al.[58]

## References

1. Rånby, B., Qu, B. J., and Shi, W. F., in *Polymer Materials Encyclopedia* (Salamone, J. C., Ed.), CRC Press, Boca Raton, FL, p. 5155 (1996).
2. Calvert, J. G., and Pitts Jr., J. N., *Photochemistry*, John Wiley & Sons, New York (1966).
3. Birkus, J. B., *Photophysics of Aromatic Molecules*, John Wiley & Sons, New York (1970).
4. *Organic Molecular Photophysics* (Birks, J. B., Ed.), Vols. 1 and 2, John Wiley & Sons, New York, Vol. 1 (1973, 1975).
5. Turro, N. J., *Modern Molecular Photochemistry*, Benjamin-Cummings, Menlo Park, CA (1978).
6. Klöpfer, W., *Introduction to Polymer Spectroscopy*, Springer Verlag, Berlin, p. 27 (1984).
7. Holden, D. A., in *Encyclopedia of Polymer Science and Engineering*, Vol. 11 (Mark, H. F., and Kroschwitz, J. I., Eds.), John Wiley & Sons, New York, p. 128 (1988).
8. Jablonski, A., *Z. Physik*, 94, p. 38 (1935).
9. Wagner, P. J., and Hammond, G. S., *Adv. Photochem.*, 15, p. 21 (1968).
10. Andrzejewska, E., private communication.
11. Guillet, J., *Polymer Photophysics and Photochemistry*, Cambridge University Press, Cambridge (1985).
12. Davidson, R. S., *Exploring the Science, Technology and Applications of U.V. and E.B. Curing*, SITA Technology Ltd., London (1999).
13. Dietliker, K., in *Chemistry and Technology of UV and EB Formulations for Coatings, Inks and Paints*, Vol. 3 (Oldring, P. K. T., Ed.), SITA Technology Ltd., London (1991).
14. Fouassier, J. P., *Photoinitiation, Photopolymerization and Photocuring*, Hanser Publishers, Munich (1995).
15. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. 1, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 15 (1998).

16. Pappas, S. P., in *Encyclopedia of Polymer Science and Engineering*, Vol. 11 (Mark, H. F., and Kroschwitz, J. I., Eds.), John Wiley & Sons, New York, p. 187 (1988).

17. Davidson, R. S., *Exploring the Science, Technology and Applications of U.V. and E.B. Curing*, SITA Technology Ltd., London, p. 67 (1999).

18. Timpe, H.-J., Miller, U., and Möckel, P., *Angew. Makromol. Chemie*, 189, p. 219 (1991).

19. Hageman, H. J., in *Photopolymerization and Photoimaging Science and Technology* (Allen, N. S., Ed.), Elsevier, Essex, England (1989).

20. Davidson, R. S., in *Polymer Materials Encyclopedia* (Salamone, J. C., Ed.), CRC Press, Boca Raton, FL, p. 7330 (1996).

21. Herlihy, S. L., and Gatesby, G. C., in *Proceedings RadTech North America*, p. 156 (1994).

22. Gruber, G. W., U.S. Patents 4,017,296 (1977) and 4,024,296 (1977) to PPG Industries.

23. Ng, H. C., and Guillet, J. E., *Macromolecules*, 11, p. 937 (1978); Wistmontski-Kittel, T., and Kilp, T., *J. Polym. Sci. Polym. Chem. Ed.*, 21, p. 3209 (1983).

24. Pappas, S. P., in *Photopolymerization and Photoimaging Science and Technology* (Allen, N. S., Ed.), Elsevier, Essex, England, Chapter 2 (1989).

25. Sahyun, M. R. V., DeVoe, R. J., and Olofson, P. M., *in Radiation Curing in Polymer Science and Technology*, Vol. II (Fouassier, J. P., and Rabek, J. F., Eds.), Elsevier, Essex, England, Chapter 10 (1993).

26. Mayer, W., Rudolf, H., and DeCleur, E., *Angew. Makromol. Chem.*, 93, p. 83 (1981).

27. Cameron, J. F., and Frechet, J. M., *J. Organ. Chem.*, 55, p. 5919 (1990), and *Pure Appl. Chem.*, 61, p. 1239 (1991).

28. Davidson, R. S., in *Polymer Materials Encyclopedia* (Salamone, J. C., Ed.), CRC Press, Boca Raton, FL, p. 7334 (1996).

29. Hageman, H. J., in *Photopolymerization and Photoimaging Science and Technology* (Allen, N. S., Ed.), Elsevier, Essex, England, Chapter 1 (1989).

30. Davidson, R. S., in *Polymer Materials Encyclopedia* (Salamone, J. C., Ed.), CRC Press, Boca Raton, FL, p. 7336 (1996).

31. Manus, P. J.-M., in *Proceedings RadTech Europe '89*, p. 539 (1989).

32. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. 1, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 21 (1998).

33. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. 1, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 22 (1998).

34. Andrzejewska, E., private communication.

35. Crivello, J. V., *Adv. Polym. Sci.*, 62, p. 1 (1984).

36. Andrzejewska, E., *Progr. Polym. Sci.*, 26, p. 605 (2001).

37. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. 1, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 2 (1998).

38. Elias, H. G., *An Introduction to Polymer Science*, VCH, Weinheim (1997).

39. Garratt, P. G., *Strahlenhärtung*, Curt Vincentz Verlag, Hannover (1996).

40. Cray Valley Product Guide (Photocure), Cray Valley, Paris, www.crayvalley.com.

41. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. 1, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 6 (1998).

42. Wittig, M., and Grohmann, Th., in *Proceedings RadTech Europe '93*, p. 533 (1993).

43. Davidson, R. S., *Exploring the Science, Technology and Applications of U.V. and E.B. Curing*, SITA Technology Ltd., London, p. 42 (1999).
44. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. 1, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 11 (1998).
45. Kohli, P., Scranton, A. B., and Blanchard, G. J., *Macromolecules*, 31, p. 568 (1998).
46. Hoyle, C., et al., ACS Symposium Series 673, p. 133 (1997).
47. Davidson, R. S., *Exploring the Science, Technology and Applications of U.V. and E.B. Curing*, SITA Technology Ltd., London, p. 46 (1999).
48. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. 1, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 8 (1998).
49. Jacobine, A. F., in *Polymer Science and Technology*, Vol. III (Fouassier, J. P., and Rabek, J. F., Eds.), Elsevier Applied Science, London, p. 219 (1993).
50. Davidson, R. S., *Exploring the Science, Technology and Applications of U.V. and E.B. Curing*, SITA Technology Ltd., London, p. 43 (1999).
51. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. 1, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 11 (1998).
52. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. 1, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 10 (1998).
53. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. 1, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 19 (1998).
54. Sheridan, M., *Industrial Paint & Powder*, 78, No. 7, July, p. 12 (2002).
55. Fouassier, J.-P., *Photoinitiation, Photopolymerization and Photocuring*, Hanser Publishers, Munich, p. 102 (1995).
56. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. 1, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 7 (1998).
57. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. 1, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 8 (1998).
58. Rånby, B., Qu, B. J., and Shi, W. F., in *Polymer Materials Encyclopedia* (Salamone, J. C., Ed.), CRC Press, Boca Raton, FL, p. 5155 (1996).
59. Chen, Y. L., and Rånby, B., *J. Polym. Sci. Part A Polym. Chem.*, 27, p. 4051 (1989).
60. Chen, Y. L., and Rånby, B., *J. Polym. Sci. Part A Polym. Chem.*, 27, p. 4077 (1989).
61. Qu, B. J., Shi, W. F., and Rånby, B., *J. Photopolym. Sci. Technol.*, 2, p. 269 (1989).
62. Reiser A., *J. Chem. Phys.*, 77, p. 469 (1980).
63. Reiser A., *Photoreactive Polymers: The Science and Technology of Resists*, John Wiley & Sons, New York (1989).
64. Hasegawa, M., in *Comprehensive Polymer Science* (Allen, G., Ed.), Pergamon, Oxford, p. 1 (1989).
65. Fouassier, P. J., in *Radiation Curing in Polymer Science*, Vol. 1 (Fouassier, J. P., and Rabek, J. F., Eds.), Elsevier, London, p. 49 (1993).
66. Jacobine, A. F., in *Radiation Curing in Polymer Science*, Vol. 3 (Fouassier, J. P., and Rabek, J. F., Eds.), Elsevier, London, p. 219 (1993).

67. Rånby, B., Qu, B. J., and Shi, W. F., in *Polymer Materials Encyclopedia* (Salamone, J. C., Ed.), CRC Press, Boca Raton, FL, p. 5159 (1996).
68. Qu, B. J., et al., Chinese Patent 912 0815889 (1991).
69. Qu, B. J., et al., Chinese Patent Application (1991).
70. Chen, Y. L., and Rånby, B., *J. Polym. Sci. Part A Polym. Chem.*, 28, p. 1847 (1990).
71. Chen, Y. L., and Rånby, B., *Polym. Adv. Technol.*, 1, p. 103 (1990).
72. Zamotaev, P. V., and Chodak, I., *Angew. Makromol. Chem.*, 210, p. 119 (1993).
73. Moussa, K., and Decker, C., *J. Polym. Sci. Part A Polym. Chem.*, 31, p. 2633 (1993).
74. Moussa, K., and Decker, C., *J. Polym. Sci. Part A Polym. Chem.*, 31, p. 2197 (1993).

# 5

## Electron Beam Processes

### 5.1 Introduction

As pointed out in Section 2.2, electrons, capable of exciting and ionizing molecules, have energies in the range of 5 to 10 eV. They are produced from fast electrons by energy degradation. As they penetrate solids and liquids, they generate ions, radicals, and excited molecules. The ionization results from inelastic collisions of fast electrons with the medium, and in the process the electrons lose energy. An empirical relationship expressing the energy of the electrons to the depth of electrons is due to Grun:[1]

$$R_G = 4.57 \ E_0^{1.75}$$

where $R_G$ is Grun range in μm and $E_0$ is the electron energy in keV.

This correlation is valid for a wide variety of materials, for polymers (e.g., polystyrene) and metals (e.g., aluminum). Thus, as the energy of the electrons increases, so does their penetration depth, and the amount of energy for high-energy electrons dissipated is small and constant over a large depth.[2] The stopping power of a material, which is the energy loss per unit path of an incident electron, depends on the density of the medium, and if it is a multi-component system, it also depends on the relative concentrations of the individual components and on their molecular weights. This is important in cases where the organic medium contains pigments, which slow down the incident electrons without yielding useful species.[3] However, the "slowed down" electrons react more readily with organic species.[4] The reactive species are dispersed randomly throughout the entire thickness of the material (see Chapter 2, Figure 2.5).

The energy deposited in the irradiated material causes a temperature rise (ΔT), which depends on absorbed dose and specific heat:

$$\Delta T = 0.239 \ D/c$$

where D is absorbed dose in kGy and c specific heat in cal/g °C of the irradiated material. Below are examples of temperature rise for different materials:

| Material | $\Delta T$ in °C/kGy |
|---|---|
| Polyethylene | 0.43 |
| Polypropylene | 0.52 |
| PVC | 0.75 |
| Aluminum | 1.11 |
| Copper | 2.63 |

Radiation processing of monomers and polymers by electron beam, such as polymerization and copolymerization of monomers, cross-linking, grafting, and degradation of polymers, is induced by these different chemically reactive species.[5–7]

Somewhat simplified, the process of interaction of high-energy electrons with organic matter can be divided into three primary events:[8]

1. *Ionization*: In this event the fast electron transfers its energy on the bonding electron in the absorbing material and the electron is knocked out. Ionization takes place only when the transferred energy during the interaction is higher than the bonding energy of the bonding electron.

$$AB \rightarrow AB^+ + e^-$$

   Practically at the same time, the ionized molecule dissociates into a free radical and a radical ion:

$$AB^+ \rightarrow A\bullet + \bullet B^+$$

   The condition for further ionization is that the knocked-out electron still has enough energy to again ionize a molecule. If the molecules are hit by electrons that do not have sufficient energy for ionization, excitation takes place.

2. *Excitation*: Excitation moves an electron from the ground state to the excited state.
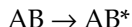
$$AB \rightarrow AB^*$$

   The excited molecule eventually dissociates into free radicals:

$$AB^* \rightarrow A\bullet + B\bullet$$
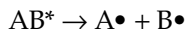
3. *Capture of electron*: This process is also ionization. Electrons with yet lower energy can be captured by molecules. The resulting ion can dissociate into a free radical and a radial ion:

$$AB + e^- \rightarrow AB^-$$
$$AB^- \rightarrow A\bullet + \bullet B^-$$
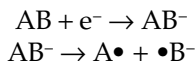
Besides these primary reactions, various secondary reactions arise in which ions or excited molecules take part.[9] The final result of these three events is

that through the diverse primary and secondary fragmentations, radicals are formed that can initiate free radical processes, leading to polymerization, cross-linking, backbone or side chain scissions, structural rearrangements, and other. The complete and rather eventful cascade of reactions triggered by the primary excitation of molecules may take up to several seconds. Under special conditions, such as when the polymer is in the glassy state or when the reactions occur in a crystalline matrix, transient species may survive for hours or even days. The energy deposited does not always cause change in the precise location where it is originally deposited, and it can migrate and affect considerably the product yield.[9] Migration of charges is another form of energy transfer in polymers, which can be electronic or ionic in nature. It can be either negative or positive and depends on temperature.[10,11] Migration of radicals has been observed in irradiated polyethylene.[12]

Although radical cations are generated in some electron-irradiated monomers (e.g., vinyl ethers or epoxies), efficient cationic polymerization is not observed.[13] Under certain conditions (addition of iodonium, sulfonium, or sulfoxonium salts, cationic polymerization with the use of electron beam irradiation can be induced.[14] Several studies on radiation cross-linking of elastomers support the concept of ionic mechanism.[15–20]

In curing applications, electrons have to penetrate the reactive solids and liquids with typical masses per unit area of one to several hundred $g/m^2$ (1 $g/m^2$ = 1 µm at unit density). As shown in the depth dose profiles in Figure 5.1,[21] electrons capable of producing any chemical change must have energies greater than 100 keV. Electrons with such energy can be generated by single-gap, low-energy electron accelerators. The *electron penetration*
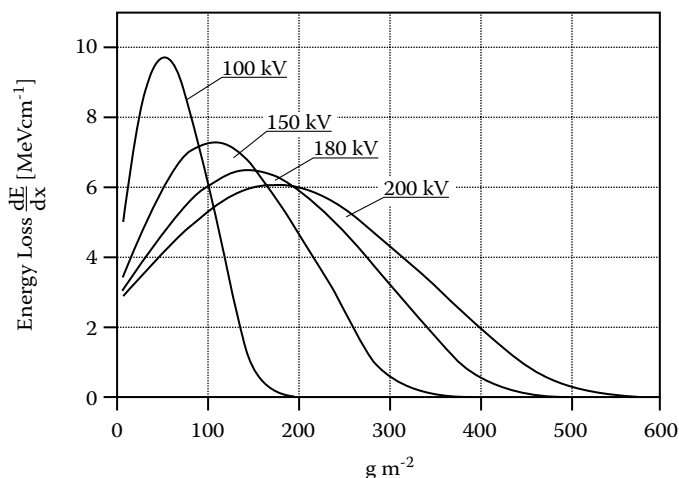


**FIGURE 5.1**
Depth dose distribution for electron energies 100–200 keV. (Tabata, T., and Ito, R., *Nucl. Sci. Eng.*, 53, p. 226 (1976). By permission of SITA Technology Ltd., UK.)

**PENETRATION PROFILES**
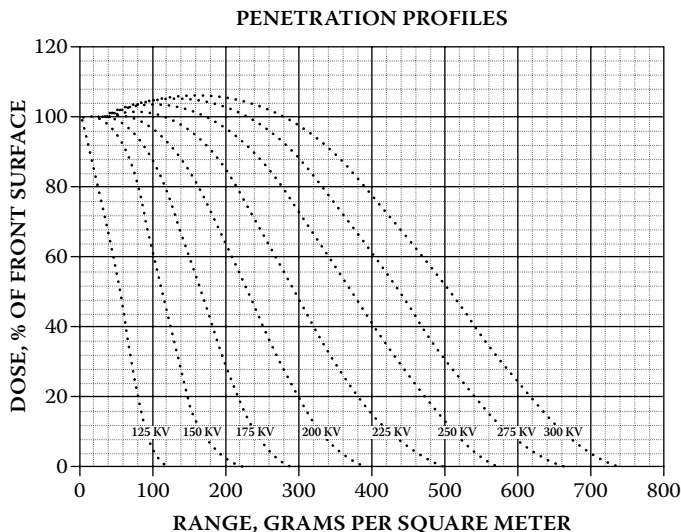


**FIGURE 5.2**
Electron penetration range in $g/m^2$ as the function of electron energy. (Courtesy of Energy Sciences, Inc.)

*range* is related to the path length the electron travels during the energy degradation process. It can be estimated from the depth dose distribution. Electron penetration range in $g/m^2$ as the function of electron energy is shown in Figure 5.2.

The reactions initiated by the formation of radicals are the most important ones in the electron beam curing process. They can be inhibited by radical scavengers, such as oxygen, which, with its unpaired electrons, is an outstanding electron acceptor and consequently a radical inhibitor. It can readily inhibit polymerization reactions proceeding by the free radical mechanism typical mainly for acrylates and other vinyl monomers. This process is particularly pronounced on the surface of a coating that is being cured by electron beam. Therefore, in practical curing applications nitrogen blanketing is used to prevent direct contact of oxygen with the surface of the material being treated by the radiation.[22]

Although there are many changes in polymeric materials induced by electron beam irradiation, there will frequently be some that will control the net changes taking place. From the practical view, the two most important are *cross-linking* and *main chain scission* (i.e., polymer degradation), since they affect the physical properties of the product. Numerous studies attempting to find answers succeeded in explaining some correlations between the structure of a polymer and its response to ionizing irradiation, but there are still many unresolved issues. Several views have been advanced that explain some of the correlations. One study[23] suggests that when the monomeric unit of the polymer contains at least one α-hydrogen, cross-linking

will take place—if not, the main chain will degrade. Another[24] proposed that vinyl polymers with two side chains attached to a single backbone carbon ($-CH_2-CR_1R_2-$) will degrade, and those with a single or no side chain ($-CH_2-CR_1H-$ or $-CH_2-CH_2-$) will cross-link. The correlation between the heat of polymerization and the tendency to degrade or cross-link was discussed by Wall.[25] Currently, the generally accepted mechanism involves the cleavage of a C–H bond on one polymer chain to form a hydrogen atom, followed by abstraction of a second hydrogen atom from a neighboring chain. The two hydrogen atoms form the $H_2$ molecule. Then the two adjacent polymeric radicals combine to form a cross-link leading to branched chains until, ultimately, a three-dimensional polymer network is formed when each polymer chain is linked to another chain. In contrast, scission is the opposite process of cross-linking in which the rupturing of a C–C bond occurs. Cross-linking increases the average molecular weight, whereas scission reduces it. If the energy of radiation is high, the chain breaks as a result of the cleavage of the C–C bond. In an oxygen atmosphere, however, the mechanistic way of scission proceeds in an indirect manner. The polymeric free radicals are generated by radiation, and the addition of oxygen to the polymeric radicals forms peroxidic species, which on decomposition form shorter chains.

It can be concluded that it is very difficult to predict the result from a polymer macrostructure, but it is relatively easy to measure the secondary species generated on irradiation by using known analytical techniques, such as measuring swelling, tensile tests, analysis using nuclear magnetic resonance (NMR), etc. The yield is then expressed by the *G value*, which represents the number of cross-links, scissions, double bonds, etc., produced for every 100 eV ($1.6 \times 10^{-17}$ J) dissipated in the material. For example, G (cross-links), abbreviated G(X), = 3.5 means that 3.5 cross-links are formed in the polymer per 100 eV under certain irradiation conditions. Similarly, the number of scissions formed is denoted by G(S). In order to determine the number of cross-links or G(X), the number of scissions or G(S), etc., it is necessary to know the dose or dose rate and the time of exposure for these irradiation conditions. From the product yields it is possible to estimate what ratio of monomer units in a polymer is affected by irradiation.[26]

For cross-linked materials, changes in cross-link density are reflected by the extent to which the material is swelled while being immersed in a compatible solvent. If cross-linking predominates, the cross-link density increases and the extent of swelling decreases. If chain scission predominates, the opposite occurs. An increased soluble fraction then reflects scission, whereas reduced soluble fraction reflects cross-linking.

For an un-cross-linked material that undergoes predominantly cross-linking when exposed to ionizing radiation, solvent extraction experiments reveal that at certain absorbed dose (the critical dose), a percentage of the material, is converted into insoluble gel. Beyond that point, the percentage of gel increases as a function of irradiation dose. In general, both the degrees of

cross-linking and scissions can be determined from the soluble fraction by using the *Charlesby-Pinner equation:*[27]

$$s + s^{1/2} = p_0/q_0 + 10/q_0\,Du_1$$

where s is the soluble fraction, $p_0$ the density of scissions per unit dose, $q_0$ the density of cross-links per unit dose, D absorbed dose in kGy, and $u_1$ the number average molecular weight. Then $p_0/q_0$ represents the ratio of chain scissions to cross-links.

The plot of $s + s^{1/2}$ vs. $1/D$ can be used to determine the $p_0/q_0$ ratio, and from that the values of G(S) and G(X) can be calculated.

Polymers can be classified into two groups according to their response to ionizing radiation. One group exhibits predominant cross-linking, the other predominant chain scission (see Table 5.1).[28]

Studies performed on elastomers have shown that the cross-linking efficiency is relatively low. G(X) values of 1 and approximately 3 were found for natural rubber and polybutadiene, respectively, when irradiated at

**TABLE 5.1**

Classification of Polymers According to Their Response to Ionizing Radiation

| Polymers Predominantly Cross-Linking | Polymers Predominantly Degrading |
|---|---|
| Polyethylene | Poly(tetrafluoroethylene) |
| Polypropylene | Poly($\alpha$-methylstyrene) |
| Polystyrene | Poly(vinylidene chloride) |
| Poly(vinyl chloride) | Poly(vinyl fluoride) |
| Poly(vinyl alcohol) | Polychlorotrifluoroethylene |
| Poly(vinyl acetate) | Polytetrafluoroethylene |
| Poly(vinyl methyl ether) | Polyacrylonitrile |
| Polybutadiene | Polyvinylbutyral |
| Polychloroprene | Poly(methyl methacrylate) |
| Copolymer of styrene and acrylonitrile | Polymethacrylonitrile |
| Natural rubber | Polyoxymethylene |
| Chlorinated polyethylene | Poly(propylene sulfide) |
| Chlorosulfonated polyethylene | Poly(ethylene sulfide) |
| Polyamides | Cellulose |
| Polyesters | Polyalanine |
| Polyurethanes | Polylysine |
| Polysulfones | Polyisobutylene |
| Polyacrylates | DNA |
| Polyacrylamides | |
| Polydimethylsiloxane | |
| Polydimethylphenylsiloxane | |
| Phenol-formaldehyde resins | |
| Urea-formaldehyde resins | |
| Melamine-formaldehyde resins | |

room temperature. Temperature was shown to have a positive effect in some cases.[29,30]

Experiments on cross-linking by irradiation have revealed that in many cases the cross-link densities equivalent to those obtained by conventional methods of cross-linking require relatively high radiation doses. Therefore, a great deal of experimental work has been done on the use of additives, which promote cross-linking by irradiation.[31] Such compounds are called radiation *cross-link promoters* or *prorads*.

## 5.2 Radiation Cross-Link Promoters

The cross-link promoters are prone to form more radicals faster than high-molecular-weight ones, and thus lower radiation doses are required to achieve required properties. There are essentially two types of promoters of radiation cross-linking or prorads.[32] One group, *indirect cross-link promoters*, does not enter directly into the cross-linking reaction, but merely enhances the formation of reactive species, such as free radicals, which then lead to secondary reactions to cross-linking. The other group, *direct cross-link promoters*, enters directly into the cross-linking reaction and becomes the actual connecting molecular links.

### 5.2.1 Indirect Cross-Link Promoters

#### 5.2.1.1 Halogenated Compounds

This group of compounds has been studied extensively,[33–41] mainly in elastomers. The findings can be summarized as follows: For chlorinated aliphatic compounds, the sensitizing effect increases with decreasing number of carbon atoms in the molecule. The cross-link promoting effect increases on passing from iodo- to bromo- to chloro-substituted compound and with increasing degree of halogenation. Halogen-containing aromatic compounds also represent good cross-linking promoters.[42]

#### 5.2.1.2 Nitrous Oxide

Enhanced radiation cross-linking in polyethylene, polypropylene, and poly-isobutylene[43] and in copolymers of ethylene and propylene[44] was found when nitrous oxide was incorporated into the polymer matrix. Mechanisms of this process have been proposed by several workers.[45–47]

#### 5.2.1.3 Sulfur Monochloride

Several investigators found a moderate[48] to substantial[49] increase in the rate of cross-linking of polyethylene and polypropylene. It was speculated that

the differences between the results of the two studies might be due to the differences in the way the promoter was distributed in the test material.[50]

### 5.2.1.4 Bases

The promotion of cross-linking of polypropylene[51] and ethylene-propylene copolymers[52] has been confirmed. However, other bases, such as amines, were not found to be effective, and in some cases they acted as retarders of radiation cross-linking.[53]

## 5.2.2 Direct Cross-Link Promoters

### 5.2.2.1 Maleimides

Maleimides and dimaleimides are known to accelerate cross-linking of elastomers by organic peroxides at elevated temperatures,[54] but they also have been found to sensitize radiation-induced cross-linking of polymers.[55,56] Experiments involving radiation cross-linking of purified natural rubber and other elastomers have demonstrated that several maleimides, alkyl-, and aryldimaleimides significantly enhance the rate of cross-linking. Among the most effective were *N*-phenylmaleimide and *m*-phenylene dimaleimide, which in amount of 5 wt.% increased the G(X) of purified natural rubber approximately by the factors of 23 and 15, respectively. The differences in the sensitizing action of the maleimides tested were at least attributed to their different solubilities in the rubber. For the *m*-phenylene dimaleimide the rate of cross-linking was found to be directly proportional to its concentration up to 10 wt.%.[56]

The mechanism of the cross-link promotion of maleimides is assumed to be based on copolymerization of the polymer via its unsaturations with the maleimide molecules initiated by radicals, and in particular, by allylic radicals produced during the radiolysis of the polymer.[55]

When tested in other polymers, maleimides did not affect the rate of cross-linking in polydimethylsiloxane, polyisobutylene, and polyvinylchloride. In polyethylene, the addition of 5 wt.% of *m*-phenylene dimaleimide increased the G(X) from 1.8 to 7.2. In the polyvinylacetate the effect was even more pronounced: the dose for gelation was reduced by about a factor of 50.[57] Contrary to the cross-link enhancing effect found for *m*-phenylene dimaleimide, cross-linking was retarded in polyvinyl acetate by the addition of monomaleimides. When analyzing the mechanism of the reaction it was concluded that monomaleimides are not expected to affect cross-linking in saturated polymers.[58]

### 5.2.2.2 Thiols (Polymercaptans)

Studies of several investigators[59–64] have shown that polyfunctional thiol compounds are useful as cross-linking agents for the radiation curing of unsaturated elastomers and polymers used in graphic arts, electronics, and coating industries. Already small amounts of these compounds enhance the

**TABLE 5.2**

Promotion of Cross-Linking by Polythiols

| Elastomer | Prorad | Prorad Amount, wt.% | G(X) Physical | Note |
|---|---|---|---|---|
| | — | — | 5 | Irradiation in air (2.5 kGy/s) |
| Polybutadiene | Dodecanethiol | 1.0 | 4.5 | Irradiation in air (2.5 kGy/s) |
| | Dimercaptodecane | 1.0 | 29 | Irradiation in air (2.5 kGy/s) |
| | Dimercaptodecane +2 wt.% *o*-dichlorobenzene | 1.0 | >49 | |
| | Dipentene dimercaptan | 1.0 | 18 | |
| | α,α'-Dimercapto-*p*-xylene | 1.0 | 39 | |
| | Trimethylolpropane trithioglycolate | 1.0 | >35 | Irradiation in air (2.5 kGy/s) |

rate of cross-linking. They also promote cross-linking of polyisobutylene and its copolymers, which normally degrade on the exposure to radiation.[65]

The basis for cross-linking in the elastomers in these studies is the addition of thiols to olefinic double bonds. This reaction has been studied by a number of investigators.[61–65] It has been shown that the addition reaction proceeds by a radical mechanism. The rate of cross-linking of polybutadiene can be strongly promoted by relatively small amounts of polythiols.[66] For example, G(X) values increased from 5 (pure polybutadiene) to 29 when 1 wt.% of dimercaptodecane was added and to more than 49 on the further addition of *o*-dichlorobenzene (see Table 5.2).

### 5.2.2.3 Acrylic and Allylic Compounds

Polyacrylic and polyallylic compounds have been found to enhance the radiation cross-linking of polyvinylchloride.[67] They were found to also accelerate cross-linking of elastomers; however, their effect is rather small.[68] Radiation cross-linking of butadiene-styrene copolymers and natural rubber compounded with 50 phr (parts per hundred parts of rubber) of carbon black[69] in the presence of acrylate promoters exhibited greatly enhanced physical properties (modulus at 300% elongation and tensile strength). The best results were attained with tetramethyl diacrylate and ethylene dimethacrylate. Several polyfunctional allylic and acrylic compounds were evaluated in the radiation cross-linking of polyethylene, polypropylene, polyisobutylene, and ethylene-propylene copolymers. The rate of gelation of these polymers was increased considerably, but many of the radiation promoters homopolymerized on

radiation exposure and, when compounded with elastomers, formed a rigid network structure within the more yielding elastomeric structure.[70–72]

## 5.3 Retardants of Radiation Cross-Linking

Compared to the interest to promote the formation of cross-links, the protection of polymers against radiation damage has received much less attention. The work that was done, however, discovered a large number of effective protective agents, often referred to as *antirads*, and also provided information on the yield of transient intermediates formed in the radiation process.[73] A considerable reduction of cross-linking was found for a number of aromatic amines, quinones, aromatic hydroxyl sulfur, and aromatic nitrogen compounds. The degree of protection offered by these compounds increases with their concentration, but reaches a limiting value at a concentration of a few weight percent.[73]

The above-mentioned radical acceptors are not the only effective protective agents against radiation. Studies performed with benzene and nitrobenzene in natural rubber[74] and styrene butadiene rubber (SBR) with *N*-phenyl-β-naphtylamine[75] demonstrated radiation protection of the respective compounds.

Many of the studied radical-accepting compounds were found to reduce the yield of scissions.[76,77] The antirads tested proved effective not only in the presence of air but also in its absence (see Table 5.3).

Different polymeric materials respond to irradiation by electron beam in different ways. A large number of them will be modified by the formation of a cross-linked network, by changing their surface properties or structure, and some will be degraded. Another field applicable to polymeric systems is polymerization and grafting. Electron beam can also be used for polymerization and cross-linking of oligomers and monomers, i.e., in conversion of liquids to solids.

## 5.4 Electron Beam Processing of Plastics

Plastics are by far the largest group of polymeric materials being processed by electron beam irradiation. Cross-linking of polyolefins, PVC, polyesters, polyurethanes, fluoropolymers, and fiber-reinforced composites is a common practice.

### 5.4.1 Polyolefins

Irradiation of polyolefins, particularly the family of polyethylenes, represents an important segment of the radiation processing. Polyolefins can be

**TABLE 5.3**

Effect of Antirads on the Yield of Cross-Links and Scissions in Natural Rubber

| Natural Rubber Compound (50 phr EPC Carbon Black) + 5 phr Antirad | G(X) | | G(S)[a] | |
|---|---|---|---|---|
| | Vacuum | Air | Nitrogen | Air |
| Control (1 phr phenyl-2-naphtylamine) | 1.9 | 0.29 | 2.7 | 13 |
| N-N'-Dicyclohexyl-p-phenylenediamine | — | — | 1.5 | 3 |
| N-Cyclohexyl-N'-phenyl-p-phenylene diamine | 1.3 | 0.33 | 1.2 | 1.4 |
| 6-Phenyl-2,2,4-trimethyl-1,2- dihydroquinoline | 0.83 | 0.19 | 1.9 | 4.2 |
| N-N'-Dioctyl-p-phenylene diamine | 0.87 | 0.12 | 1.5 | 5.0 |
| 2-Naphtylamine | 0.87 | 0.30 | 1.6 | 5.6 |
| p-Quinone | — | — | 2.8 | 7.8 |
| Phenylhydroquinone | 1.1 | 0.46 | 2.2 | 5.4 |
| 1,4-Naphtoquinone | 1.1 | 0.48 | 2.0 | 5.6 |
| 2-Naphtol | 1.1 | 0.24 | 1.3 | 4.1 |
| N-N'-Diphenyl-p-phenylenediamine (35%) and phenyl-1-naphtylamine (65%) | 0.97 | 0.27 | 1.4 | 3.7 |

[a] Scission yields are determined by stress relaxation measurements during irradiation of specimens. Permanent and temporary chain scissions are measured by this technique in contrast to gel measurements, which provide data only on permanent scissions.

irradiated in many forms, such as pellets and powders, films, extruded and molded parts, or as wire and cable insulation.

Pellets and powders, as well as small parts, are handled simply by conveyor belts; cart systems or air transport tubes are the most common transportation systems for continuous electron beam irradiation.[78] Wire and cable as well as tubular products require special handling. Frequently, irradiation from one side is not sufficient since it results in nonuniform dose distribution. Therefore, the product has to be twisted so that its entire circumference is presented to the source of irradiation. Multiple passing is another way to alleviate this problem. Details are in the Section 8.1 on wire and cable and Section 8.4 on heat-shrinkable products. Thick sheets and extruded profiles have to be often irradiated from both sides passing under the beam several times. Large and thick parts require spinning along some predetermined axis or angle to ensure uniform dose distribution.[78]

### 5.4.1.1 Polyethylene

The effects of ionizing radiation on polyethylene in all its forms can be summarized as follows:[79]

- The evolution of hydrogen
- The formation of carbon-carbon cross-links

- An increase in unsaturation to an equilibrium level
- A reduction in crystallinity
- The formation of color bodies in the resin
- Surface oxidation during irradiation in air

The formation of carbon-carbon cross-links is by far the most important effect and is the basis of the applications in wire and cable industry and for heat-shrinkable products. The factors affecting the changes of polyethylene by irradiation are the molecular weight distribution, branching, degree of unsaturation, and morphology.[80]

Low-density polyethylene (LDPE), produced by a high-pressure polymerization, contains long branches attached to the main chain. Linear low-density polyethylene (LLDPE) has a rather regular succession of short-chain branches. Both types have a small amount of unsaturation, but high-density linear polyethylene (HDPE) contains one terminal vinyl group per molecule. At low radiation doses, this vinyl group has the effect of increasing the molecular weight of the HDPE by the chain formation of Y-links between the vinyl and the secondary alkyl radicals produced by the radiation.[81]

At ambient temperatures, polyethylene is always in the semicrystalline form. The amorphous region has a density of 800 kg/m$^3$ (50 lb/ft$^3$); the density of the crystalline region is 25% greater. The range of commercially available polyethylenes is from 920 to 960 kg/m$^3$ (58 to 60 lb/ft$^3$), but this relatively small difference in density corresponds to a considerably greater difference in the amorphous fraction: its weight fraction in LDPE is 40% and about 20% in HDPE.[82] The cross-linking takes place mainly in the amorphous region and the interface between the two phases. The cores of the crystalline regions sustain radiation-induced transvinylene formation in proportion to their weight fraction, but they are scarcely involved in gel formation.[82] Radiation cross-linking effects and the degree of cross-linking within crystalline regions are reported in the literature.[83–87]

Cross-linking of polyethylene by irradiation takes place normally at temperatures below 70°C (158°C), which is below its alpha transition temperature and much lower than the crystalline melting point. The irradiation does not have any significant effect on sizes of amorphous and crystalline fractions as measured by the heats of fusion. However, when the cross-linked polymer is heated above the crystalline melting point, the crystallinity is significantly reduced because the cross-links interfere with the reformation of the supermolecular fraction during cooling from the melt. Subsequent cycles of melting and cooling do not produce additional changes in crystallinity.[82,87,88]

The core of the crystalline region of irradiated PE contains residual free radicals. These diffuse slowly to the interface with the amorphous region,

where, in the presence of dissolved oxygen, whose equilibrium concentration is maintained by diffusion, they initiate auto-oxidative chain of degradation.[89] Postirradiation annealing in an inert atmosphere at a temperature above the alpha transition temperature (85°C or 185°F) leads to rapid mutual reactions of the free radicals and eliminates the problem.[90]

The higher crystalline fraction of the radiation cross-linked polyethylene even after a melt-freeze cycle has great technological merit for the heat-shrink packaging and electrical connector products.[91,92]

Compared with chemical cross-linking of PE, radiation curing produces a different product in many respects. The chemical cross-linking is done at temperatures near 125°C (257°F), where the polymer is in the molten state. Consequently, the cross-link density in the chemically cross-linked polyethylene is almost uniformly distributed, while there are relatively few cross-links in the crystalline fraction of the radiation cross-linked PE. The crystalline fraction of the radiation-processed polyethylene is greater than that in the chemically cured product.[82]

Radiation cross-linking of polyethylene requires considerably less overall energy and less space, and is faster, more efficient, and environmentally more acceptable.[93] Chemically cross-linked PE contains chemicals, which are by-products of the curing system. These often have adverse effects on the dielectric properties and, in some cases, are simply not acceptable.[94]

The disadvantage of electron beam cross-linking is a more or less nonuniform dose distribution. This can happen particularly in thicker objects due to intrinsic dose-depth profiles of electron beams. Another problem can be a nonuniformity of rotation of cylindrical objects as they traverse a scanned electron beam. However, the mechanical properties often depend on the mean cross-link density.[95]

### 5.4.1.2 Polypropylene

Polypropylene (PP) is a stereospecific polymer prepared by polymerization using an organometallic catalyst system. Commercial polypropylenes have up to 95% isotactic content, which means that pendant methyl groups are almost all on the same side of the chain.

When polypropylene is exposed to ionizing radiation, free radicals are formed and these cause chemical changes. Since PP is highly crystalline, these radicals are relatively immobile, and consequently may not be available for reaction for long periods of time.[96]

As with other polyolefins, upon irradiation the free radicals are formed along with evolution of hydrogen gas. If the radical is formed on the pendant methyl, the resulting reaction is cross-linking. However, if the radical is formed in the main chain, the chain end may react with hydrogen, thus causing an irreversible scission. Although the processes of chain scission and

cross-linking occur simultaneously, and even though the net effect is cross-linking, the overall effect is the loss of mechanical strength.[97]

### 5.4.2 Polystyrene

Polystyrene is a clear, amorphous polymer with a high stiffness and good dielectric properties. It is easily cross-linked by ionizing radiation. Often small amounts of divinyl benzene may enhance the degree of cross-linking.[98]

Moderate doses, between 1.0 and 20 Mrad (10 to 200 kGy) on partially or completely formed articles and polymer pellets, substantially reduce the content of residual monomer.[98] The mechanical properties of polystyrene are changed only at high radiation doses, which is characteristic of low cross-link yield and glassy morphology.[99]

### 5.4.3 Polyvinylchloride

Polyvinylchloride (PVC) is a slightly crystalline polymer, because of its branched structure. A large amount of PVC is for insulations in the wire and cable industry. Radiation cross-linking of PVC requires the addition of a multifunctional prorad. In the absence of air, cross-linking predominates over chain scission and $G(X) = 0.33$. Addition of plasticizers or rising temperature above the glass transition increases cross-link yield.[100] Irradiated PVC materials usually show an increase in solvent, heat, and flow resistance.[101] Radiation curable PVC and its copolymers are suitable for grafting involving multifunctional monomers.[102]

The most effective prorads for PVC are acrylic and allylic esters, such as triallyl cyanurate (TAC), trimethylolpropane trimethacrylate (TMPTMA), and trimethylolpropane triacrylate. The triacrylate is more reactive than the trimethacrylate, but it is more toxic and, for that reason, is used only seldom. The amounts of these additives are 1 to 5% of the formulation weight.[103]

### 5.4.4 Polymethacrylates and Polyacrylates

Polymethyl methacrylate (PMMA) degrades under irradiation and becomes more soluble due to main chain scission.[104] The degradation can be greatly reduced by the addition of 10% of various additives, such as aniline, thiourea, or benzoquinone.[105] PMMA is an example of a nongelling polymer; it does not form a three-dimensional network structure under irradiation.[106]

### 5.4.5 Polyamides

In general, copolymers cross-link more readily than polyamide PA 66. Mechanical properties of polyamides are modified by irradiation, as seen by reduced tensile strength (50% loss when irradiated in air, 16% under vacuum). Aromatic polyamides retain strength better than aliphatic polyamides.[99]

### 5.4.6 Polyesters

Aliphatic polyesters tend to cross-link upon irradiation. Poly(ethylene terephtalate) cross-links with a low efficiency; however, it can sustain desirable physical properties up to 0.5 MGy.[99]

### 5.4.7 Fluoroplastics

#### 5.4.7.1 Polytetrafluoroethylene

Under normal conditions polytetrafluorothylene (PTFE) undergoes chain scission. In fact, this behavior is exploited commercially by converting PTFE scrap into a low-molecular-weight product that is then used in the form of very fine powders as additive to inks and lubricants. However, there is evidence that irradiation of PTFE at temperatures above its melting point (e.g., at 603–613 K, or 626–644°F) in vacuum results in a significant improvement in tensile strength and elongation at 473 K (392°F) and in the tensile modulus at room temperature.[107–109] These findings strongly contrast with the greatly reduced properties after irradiation at lower temperatures than that. This clearly indicates cross-linking in the molten state, similar to effects of irradiation on polyethylene. At temperatures above 623 K (662°F), thermal depolymerization is increasingly accelerated by irradiation and predominated over cross-linking at yet higher temperatures.[110]

When PTFE is degraded by ionizing radiation under vacuum, the amount of toxic compounds, such as HF and CO, decreases. The threshold value of absorbed dose for vacuum degradation of PTFE was found to be about 50–60 kGy.[111]

#### 5.4.7.2 FEP

FEP, copolymer of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP), has physical and chemical properties similar to those of PTFE, but it differs from it in that it can be processed by standard melt processing techniques.

When FEP is exposed to ionizing radiation at ambient temperature, it degrades like PTFE, with resulting reduction of physical properties. However, if the temperature of the polymer is raised before irradiation above its glass transition temperature, cross-linking predominates and manifests itself by the increase in viscosity. With doses greater than 2.6 Mrad (26 kGy), ultimate elongation and resistance to deformation under load at elevated temperatures are improved, and the yield stress is increased. However, the improvements are offset by some loss in toughness.[112]

#### 5.4.7.3 Other Fluoroplastics

*Polychlorotrifluoroethylene* (PCTFE), according to one source, degrades upon ionizing irradiation in a similar fashion as PTFE at ambient and elevated

temperatures.[113] Unlike PTFE, when irradiated above its crystalline melting point, it still exhibits chain scission.[113] However, the resistance of PCTFE to ionizing radiation is reported to be better than that of other fluoropolymers.[113]

The copolymer of *ethylene and tetrafluoroethylene* (ETFE) can be cross-linked by irradiation.[114] Further improvement is achieved with the use of prorads, such as TAC or TAIC, in amounts up to 10%.

The copolymer of *ethylene and trichlorofluoroethylene* (ECTFE) behaves upon irradiation like ETFE, including improvement of cross-linking efficiency with prorads.

*Polyvinylidene fluoride* (PVDF) and *polyvinyl fluoride* (PVF) cross-link upon irradiation, particularly with the use of prorads, such as TAC, TIAC, diallyl itaconate, ethylene bis-maleimide, and others.[113]

## 5.5 Electron Beam Processing of Elastomers

Elastomers are polymeric substances with rubber-like behavior at ambient temperatures. This means they are more or less elastic, extensible, and flexible. They can be extended by relatively small force and return to the original length (or near it) after the force is removed. Rubber-like behavior can be observed in plastics, but under different conditions, such as at elevated temperatures or in swollen state. These are not true elastomers, however.

The macromolecules of elastomers are very long and flexible, randomly agglomerated and entangled; the entangled macromolecular chains produce mechanical knots. Secondary forces acting between molecules are about a hundred times weaker than the primary bonds between the atoms connected within the molecule. The secondary forces are of physical nature, and their strength decreases rapidly with increasing distances between the molecules and with increasing temperature. The arrangement of the elastomeric molecules (flexibility and coiling of the chains, relatively weak intermolecular forces, chain entangling, and mechanical knots) gives elastomers the ability to undergo reversible deformations, but only under certain conditions: the deformation should not be too large and should last only a short time and within a narrow temperature interval. At higher deformations, particularly at elevated temperatures, the chains start to slide, the entanglements are reduced, and a permanent deformation takes place. The time dependence of these changes indicates a viscoelastic behavior of such polymeric material. The mechanical knots formed by the chain entanglements are not permanent, and the weak intermolecular forces cannot guarantee a sufficient shape stability of the material because they are affected by the changes of physical conditions (temperature, swelling) and they come into play only at low temperatures. Such material has only limited technical applications, because it has poor mechanical properties and sensitivity to temperature changes. It is predominantly plastic and dissolves in some liquids to give colloidal solutions.
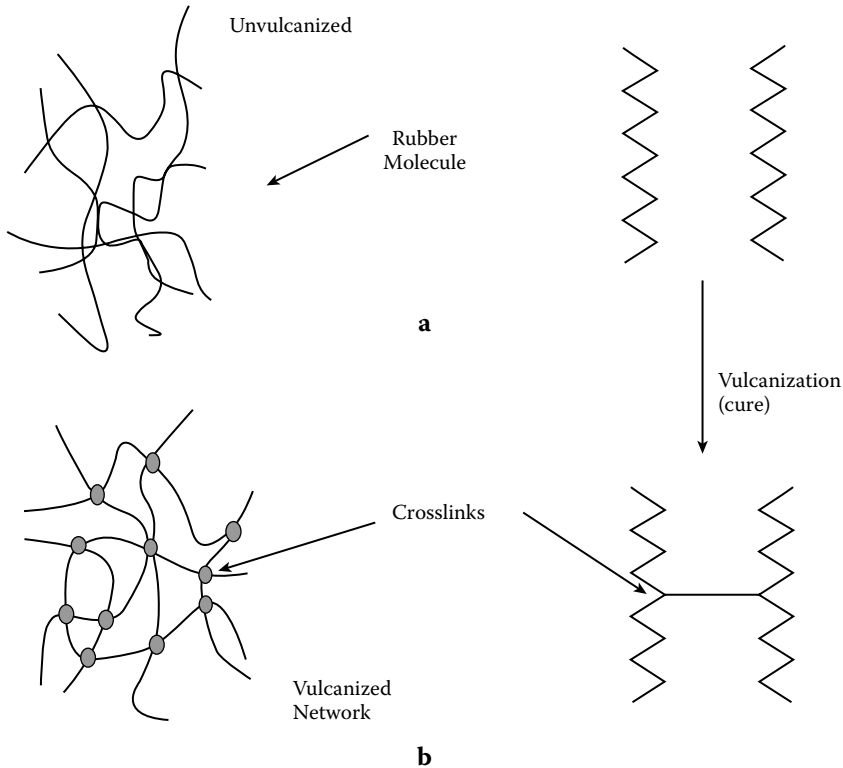
**FIGURE 5.3**
Elastomeric material: (a) un-cross-linked and (b) cross-linked.

Only when chemical bonds between neighboring molecules are introduced is a raw elastomer converted into a rubber vulcanizate, which is essentially a three-dimensional network structure (see Figure 5.3). The process is referred to as vulcanization or curing, or more accurately, as cross-linking. A cross-linked elastomer, or rubber vulcanizate, is capable of large reversible deformations within a broad temperature range and does not dissolve, but only swells in solvents and other liquids.

There are a large number of elastomeric materials used in commercial applications. They differ in the chemical nature of the monomer units, in their mutual arrangement and bonding, molecular weight, molecular weight distribution, branching, gel amount, etc. All these factors determine their chemical and physical properties, processing behavior, and solubility. Practically all commercial elastomers have a glass transition temperature below 0°C (32°F), and their molecular weights can range from 10,000 to 1,000,000.[115]

*Vulcanization* or cross-linking of elastomers is technically the most important process for conventional elastomers. During that process strong chemical

bonds are formed between molecules restraining their mobility. As pointed out earlier, a three-dimensional network is formed. The cross-linking of elastomeric molecules is a random process; typically one cross-link is formed per one hundred to two hundred monomeric units.

The following changes occur as a result of cross-linking:

- The material changes from a plastic to elastic state.
- The product is much less sensitive to temperature changes.
- The material becomes stronger and often harder.
- The shape fixed by vulcanization (e.g., in a compression mold) cannot be changed unless it is subjected to mechanical work.

There are several methods of vulcanizing standard commercial elastomers. The classic method involves sulfur or sulfur-bearing compounds and peroxides, and these are typically used for hydrocarbon elastomers, such as natural rubber, styrene-butadiene rubber, polybutadiene rubber, EPM, and EPDM. Other elastomers, such as polychloroprene, other chlorine-bearing elastomers, polyurethanes, and fluorinated rubber, use specific curing systems. Details about curing methods, compounding, and processing are covered in detail in several monographs.[116–119]

Regardless of the method of cross-linking, mechanical properties of a cross-linked elastomer depend on cross-link density. Modulus and hardness increase monotonically with cross-link density, and at the same time, the network becomes more elastic. Fracture properties, i.e., tensile and tear strength, pass through a maximum as the cross-link density increases (see Figure 5.4).
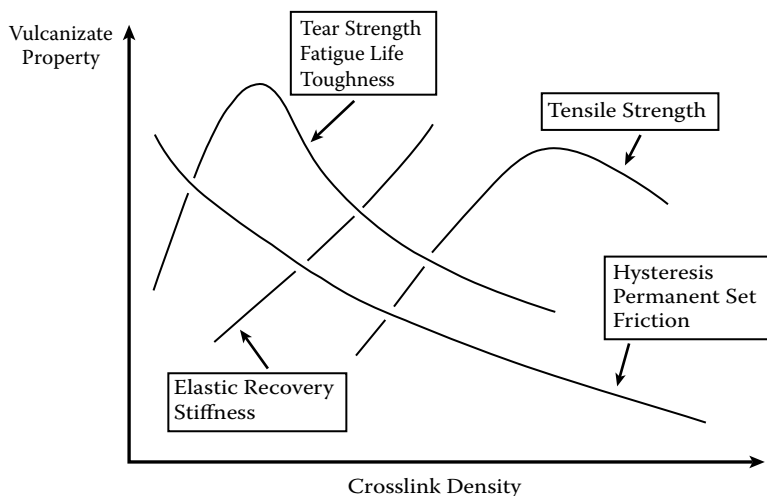


**FIGURE 5.4**
Effect of cross-link density on selected properties of an elastomeric material.

The cross-link density can be determined by equilibrium swelling or from equilibrium stress-strain measurements at low strain rate, elevated temperature, and sometimes in the swollen state.[120]

As pointed out earlier, an elastomer cross-linked above its gel point will not dissolve in a solvent, but will absorb it and swell. The swelling will continue until the forces of swelling balance the retroactive forces of the extended chains of the network. The cross-link density can then be calculated from the degree of swelling using the *Flory-Rehner equation*:

$$N = \frac{1}{2V_s} \frac{\ln(1 - \phi + \phi + \chi\phi^2)}{\phi^{1/3} - \phi/2} \tag{5.1}$$

where $N$ = moles of cross-links per unit volume (cross-link density), $V_s$ = molar volume of the solvent, $\phi$ = volume fraction of polymer in the swollen gel, and $\chi$ = polymer-solvent interaction parameter.

When using equilibrium stress-strain measurements, the cross-link density is determined from the *Mooney-Rivlin equation*:

$$\sigma/2(\lambda - \lambda^{-2}) = C_1 + C_2/\lambda \tag{5.2}$$

where $\sigma$ = engineering stress (force per unit of original cross-sectional area), $\lambda$ = extension ratio (measured length to original length), and $C_1$, $C_2$ = constants.

The value of $C_1$ is obtained from the plot of $\sigma/2(\lambda - \lambda^{-2})$ vs. $1/\lambda$ and extrapolating to $1/\lambda = 0$. By comparison with the theory of elasticity, it has been proposed that $C_1 = 1/2$ NRT, where N is cross-link density, R the gas constant, and T the absolute temperature (of the measurement). To assure near-equilibrium response, stress-strain measurements are carried out at low strain rate, elevated temperature, and sometimes in the swollen state.[120]

## 5.5.1 Physical Properties of Radiation Cross-Linked Elastomers

Identical to chemically cross-linked (vulcanized) elastomers, the modulus of radiation cured gum elastomers depends on the concentration of elastically effective network strands and temperature.[121]

Generally, values of tensile strength of radiation cured elastomers are reported to be lower than those of sulfur cured rubber.[122] It can be shown that main chain scissions, prevalent particularly under certain irradiation conditions, have a distinct effect on the strength of cured elastomers. The effect can be understood in terms of reduction in molecular weight and an associated increase in the chain-end contribution.[123] If a certain modulus is to be achieved in a vulcanizate, regardless of whether or not scission is occurring, the increase in chain ends (chains that have no load-bearing capacity) has to be compensated by an increase in the number of chemical cross-links. The associated decrease in the molecular weight of an elastically active strand ($M_c$) and its effect on failure properties such as energy to break were shown

**TABLE 5.4**

Comparison of Stress-Strain Properties of Natural Rubber Cross-Linked by Sulfur and Radiation

| Gum (Compound Without Fillers) | Sulfur Cured | Radiation Cured |
|---|---|---|
| Tensile strength, MPa (psi) | 27.8 (4,026) | 18.6 (2,700) |
| Elongation at break, % | 700 | 760 |
| 300% modulus, MPa (psi) | 2.3 (332) | 1.7 (250) |
| **Reinforced by 50 phr HAF Carbon Black** | **Sulfur Cured** | **Radiation Cured** |
| Tensile strength, MPa (psi) | 27.4 (3,975) | 22.8 (3,300) |
| Elongation at break, % | 470 | 350 |
| 300% modulus, MPa (psi) | 14.8 (21.50) | 17.9 (2,600) |

in Flory.[123] Since the maximum observable extension ratio $[(l/l_o)_{max}]$ is proportional to $M_c$, the increase in G(S)/G(X) encountered during radiation cure should decrease the $[(l/l_o)_{max}]$, and consequently cause lower failure properties, such as tensile strength, energy to break, etc.[124,125]

There are certain polymers, such as polyisobutylene, which by nature of their microstructure have a high yield of radiation-induced scissions, regardless of how they were irradiated. However, even polymers for which G(S) is negligible, when irradiated *in vacuo*, will undergo main chain scissions if the exposure is carried out at high temperature, in the presence of oxygen or certain additives. Degradation can also become significant with polymers having a low yield of cross-links G(X), since in the presence of a modest scission rate, the ratio G(S)/G(X) can be of significant magnitude.[126] The compound ingredients, such as antioxidants, oils, etc., may retard the rate of cross-linking of an elastomeric compound. Thus, the presence of cure-retarding impurities and the exposure in an atmosphere containing oxygen may significantly contribute to the lower strength of radiation cured elastomers. Another factor may be degradation of the polymer by ozone generated during irradiation.

Obviously, there are many subtle differences in the structure, morphology, or network topology between radiation cured and sulfur cured elastomers,[127] but their physical properties may be nearly equal, provided that precautions are taken to avoid the occurrence of chain scissions. A comparison of radiation cross-linked and sulfur cured natural rubber (gum and carbon-black-reinforced compounds) is in Table 5.4.[128,129]

## 5.5.2 Effects of Radiation on Individual Elastomers

### 5.5.2.1 Natural Rubber (NR) and Synthetic Polyisoprene

Natural rubber and guttapercha consist essentially of polyisoprene in *cis*-1,4 and *trans*-1,4 isomers, respectively. Commercially produced synthetic polyisoprenes have more or less identical structures but reduced chain regularity, although

some may contain certain proportions of 1,2 and 3,4 isomers. Microstructure differences not only cause the polymers to have different physical properties, but also affect their response to radiation. The most apparent change in microstructure on irradiation is the decrease of unsaturation. It is further promoted by the addition of thiols and other compounds.[130] On the other hand, antioxidants and sulfur were found to reduce the rate of decay of unsaturation.[131] A significant loss in unsaturation was found particularly in polyisoprenes composed primarily of 1,2 and 3,4 isomers.[132,133]

A very important process occurring during irradiation is the formation of free radicals that leads to other changes, such as cross-linking, polymerization reactions, and grafting.

### 5.5.2.1.1 Gas Evolution

About 98% of gas formed during radiolysis of natural rubber and polyisoprene is hydrogen, the rest consists of methane and higher-molecular-weight hydrocarbons. The yield of hydrogen is directly proportional to dose up to 200 Mrad (2,000 kGy). Moreover, it is independent of dose rate and the type of radiation (gamma, electron beam).[134]

### 5.5.2.1.2 Cross-Linking

Cross-linking of natural rubber and synthetic polyisoprene has been studied by several investigators using electron beam and gamma radiation.[135–137] The general conclusion is that the yield of chemical cross-links, G(X), is constant with dose and independent of dose rate and the type of radiation used.[137] Effects of temperature are reported in Böhm and Tveekrem.[138]

The yield of cross-links in natural rubber and in high *cis*-polyisoprenes was found to be about equal; however, polyisoprenes with high 1,2 and 3,4 configurations exhibited exceptionally high G(X). The presence of 1,4 units contributed to the occurrence of chain scissions.[139,140] Oxygen has been found to increase the rate of scission and to decrease the degree of cross-linking.[134,141] Another interesting finding was that the rate of cross-linking is enhanced in crystalline domains produced by strain orientation.[141] Maleimides and some halogenated compounds enhance the cross-linking of natural rubber (see Section 5.2).

### 5.5.2.1.3 Physical Properties

The most commonly reported physical properties of radiation cross-linked natural rubber and compounds made from it are modulus and tensile strength, obtained from stress-strain measurements. Figure 5.5 illustrates some of the results obtained from gum rubber and from a natural rubber compound reinforced by HAF carbon black.[141] In Figure 5.6 the tensile strength of radiation cured gum is compared to that of vulcanizates cured by sulfur and by peroxide.[142]

Clearly, large doses are required for a full cure. The dose levels for attaining a maximum tensile strength are within 20 to 50 Mrad (200 to 500 kGy).
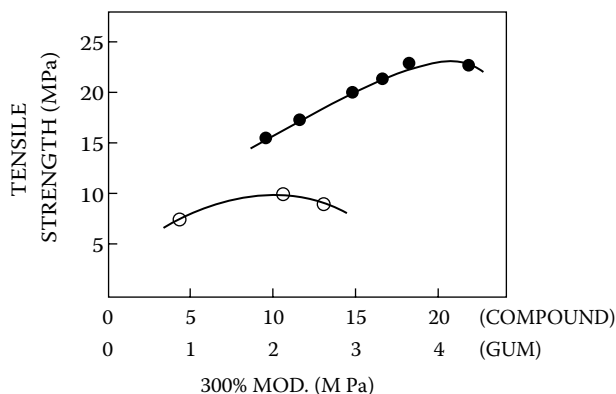
**FIGURE 5.5**
Tensile strength of radiation cured purified natural rubber. o, gum; •, compound (50 phr N330 carbon black). (Böhm, G. G. A., and Tveekrem, J. O., *Rubb. Chem. Technol.*, 55: 3, p. 619. Reprinted with permission from Rubber Division, ACS.)

After exposure to such high levels of radiation, considerable modifications of natural rubber by isomerization and chain scission processes occur.[143] Because of that, the maximum strength values of gum rubber achieved by ionizing radiation are lower than those achieved by sulfur and peroxide curing systems. When prorads (cross-link promoters), such as dichlorobenzene, maleimides, or acrylates, are used, the curing dose is reduced and higher tensile strength values are found. Tensile strength data from radiation cured NR are in Table 5.5.

Somewhat greater tensile strength and elongation at break are obtained with high-energy electrons than with gamma radiation, when exposure is
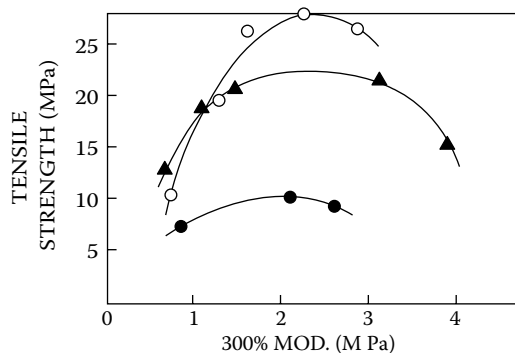


**FIGURE 5.6**
Tensile strength of radiation cured purified natural rubber. o, sulfur; Δ, peroxide; •, EB irradiation in nitrogen at 2.5 kGy/s. (Böhm, G. G. A., and Tveekrem, J. O., *Rubb. Chem. Technol.*, 55: 3, p. 620. Reprinted with permission from Rubber Division, ACS.)

**TABLE 5.5**

Tensile Strength Data from Electron Beam Cured Natural Rubber

| Compound | Amount of Additive, phr | Dose, kGy | Tensile Strength, MPa (psi) Reported | Note |
|---|---|---|---|---|
| Gum rubber (SMR-5L) plus *o*-dichlorobenzene | 3 | 140 | 9.0 (1,305) | 15 kGy/s |
| Gum rubber (smoked sheets) | — | 600 | 4.8 (696) | Irradiated in air |
| Smoked sheets and N330 carbon black | 50 | 500 | 19.6 (2,842) | Irradiated in air |
| | | 140 | 13.3 (1,928) | |
| Smoked sheets and N330 carbon black plus octyl acrylate | 60 | 140 | 18.3 (2,654) | Irradiated in air |
| | 20 | | | |
| Smoked sheets and N330 carbon black plus tetramethylene diacrylate | 55 | 140 | 18 (2,291) | Irradiated in air |
| | 10 | | | |
| Smoked sheets and N330 carbon black plus glyceryl triacrylate | 50 | 130 | 16.6 (2,407) | Irradiated in air |
| | 5 | | | |
| Pale crepe and N330 carbon black | 50 | 160 | 15.8 (2,291) | Irradiated in air |
| Pale crepe and N330 carbon black plus octyl acrylate | 50 | 160 | 16.6 (2,407) | Irradiated in air |
| | 20 | | | |

carried out in air. However, when antioxidants are added to the compound, the differences diminish.[141,143]

The retention of the maximum tensile strength at elevated temperatures is greater for radiation cured than for chemically cured natural rubber.[144–146] The physical properties after high-temperature aging are not improved, however. Lower flex life and higher abrasion resistance of radiation cross-linked NR were reported.[147] Other properties, such as permanent set, hardness, and resilience, were found to be nearly equal.

### 5.5.2.1.4  Natural Latex

The prevulcanization of natural rubber in latex form has also been a subject of much investigation.[148] The cross-linking mechanism is not yet fully understood, but the water apparently plays a major role in it. Irradiation results in the cross-linking of the rubber molecules and in coarsening of the latex particles. A process of cross-linking of natural rubber latex has been developed to the point that it can be used for an industrial-scale application.[148] The irradiation is performed in aqueous media by electron beam without a prorad (sensitizer) at a dose of 200 kGy (20 Mrad) or in the presence of *n*-butyl acrylate at considerably lower doses, typically 15 kGy. The cross-linked film exhibits physical properties comparable to those obtained from sulfur cured (vulcanized) film. As an alternative, the addition of a variety of chloroalkanes makes it possible to achieve a maximum tensile strength with radiation doses of less than 5 Mrad (50 kGy).[148]

### 5.5.2.2  Polybutadiene and Its Copolymers

Homopolymers of polybutadiene can consist of three basic isomeric forms (*cis*-1,4, *trans*-1,4, and 1,2 vinyl), and these can be present in different sequential order. Copolymers may obtain a variety of co-monomers, such as styrene, acrylonitrile, etc. Depending on their distribution in the chain, random copolymers or block copolymers of different types and perfection can be produced. There are many synthetic elastomers based on butadiene available commercially.

Upon irradiation, 1,4 polybutadienes and poly(butadiene-styrene) form free radicals relatively readily, and their concentration has been found to increase linearly proportional to dose up to approximately 100 Mrad (1,000 kGy).[149]

### 5.5.2.2.1  Gas Evolution

During radiolysis of polybutadiene and butadiene-styrene copolymers hydrogen and methane evolve.[150–157] The incorporation of styrene as co-monomer strongly reduces the total gas yield. Small amounts (typically 2 phr) of *N*-phenyl-β-naphtylamine greatly reduce the gas yield[150] and at the same time reduce G(X) considerably.

### 5.5.2.2.2 Changes in Microstructure

Similar to NR, polybutadiene and its copolymers exhibit decay of unsaturation during radiolysis. Its extent depends greatly on microstructure.[155,157] Another effect observed is *cis-trans* isomerization.[157,158]

### 5.5.2.2.3 Cross-Linking

The yield of cross-links depends on the microstructure and purity of the polymer as well as whether it was irradiated in air or *in vacuo*.[146] The rate of degradation was found to be essentially zero when polybutadiene or poly(butadiene-styrene) was irradiated *in vacuo*, but increased somewhat when irradiated in air.

   The cross-linking of polybutadiene and its copolymers can be greatly enhanced by the addition of direct or indirect cross-link promoters. The largest G(X) values are obtained when using polymercaptans in combination with halogenated aromatics.[153,160,161] Carbon blacks and silica fillers were found to enhance cross-linking and, to some extent, become chemically linked to the polymer chain.[162,163] Some investigators suggest that electron beam irradiation of carbon-black-reinforced rubber compounds results in an increased cross-link density near the surface of the carbon black particle.[164] Aromatic oils enhance the occurrence of chain scissions and decrease the rate of cross-linking.[165] Common accelerators for rubber, such as tetramethylthiuram disulfide, sulfur, diphenylguanidine, and mercaptobenzothiazole, inhibit radiation cross-linking, the degree of retardation being in the order of their listing.[155] As pointed out previously, several chemicals were reported to protect polybutadiene and its copolymers against radiation damage.

   The reactions leading to the formation of cross-links between polymeric chains also can be employed to attach various compounds to the polymeric backbone. Using this technique, grafting of styrene,[166] mercaptans,[167] carbon tetrachloride,[167,168] and other compounds can be carried out.

### 5.5.2.2.4 Physical Properties

The information on physical properties of radiation cross-linking of polybutadiene rubber and butadiene copolymers was obtained in a fashion similar to that for NR, namely, by stress-strain measurements. From Table 5.6, it is evident that the dose required for a full cure of these elastomers is lower than that for natural rubber. The addition of prorads allows further reduction of the cure dose with the actual value depending on the microstructure and macrostructure of the polymer and also on the type and concentration of the compounding ingredients, such as oils, processing aids, and antioxidants in the compound. For example, solution-polymerized polybutadiene rubber usually requires lower doses than emulsion-polymerized rubber because it contains smaller amount of impurities than the latter. Since the yield of scission G(S) is relatively small, particularly when oxygen is excluded, tensile

**TABLE 5.6**
Tensile Strength Data from Electron Beam Cross-Linked Polybutadiene and Its Copolymers

| Polymer | Co-monomer, mol% | Additive | Amount of Additive(s), phr | Dose, kGy | Tensile Strength, MPa (psi) Reported |
|---|---|---|---|---|---|
| Polybutadiene | 0 | N330 carbon black and p-dichlorobenzene | 50 2 | 80 | 15.2 (2,204) |
| Poly(butadiene-styrene) | 22.5 | N330 carbon black and p-dichlorobenzene | 50 2 | 100 | 23.45 (3,400) |
| | 23.5 | N330 carbon black | 50 | 280 | 20.4 (2,958) |
| | 25 | N330 carbon black | 50 | 400 | 19.2 (2,784) |
| | | N330 carbon black plus hexachloroethane | 50 3 | 150 | 18.1 (2,624) |
| Poly(butadiene-acrylonitrile) | 32 | Semireinforcing carbon black | 50 | 100 | 22 (3,190) |

strengths comparable to those attainable with standard sulfur cured systems are obtained.[169] Radiation cured polybutadiene and its copolymers were reported to have superior tensile strength and ultimate elongation at high temperatures.[170] The abrasion resistance was found to be higher; most of the higher properties, such as hardness, resilience, and permanent set, were equal to those of chemically cured compounds of this category. Tensile strength values near equal to those obtained by chemically cured nitrite-butadiene rubber (NBR) were reported.[147,171,172] Relatively low radiation doses were required for a complete cure of these materials. Radiation cured carbon-black-reinforced styrene-butadiene rubber (SBR) was found to have somewhat lower tensile strength and a lower maximum extensibility than sulfur cured compounds, considerably longer fatigue flex life, and slower crack growth.[146]

### 5.5.2.3 Polyisobutylene and Its Copolymers

To this category belong homopolymers of polyisobutylene, copolymers of isobutylene and isoprene (butyl rubber), chlorobutyl, and bromobutyl. All these have been produced commercially for decades.

Upon irradiation, polyisobutylene and its copolymers tend to degrade. There are a large number of studies determining the nature of the process and mechanisms, and it was established that it involves formation and reaction of free radicals.[173] The radical concentration increases linearly with a dose up to 100 Mrad (1,000 kGy).[174]

#### 5.5.2.3.1 Gas Evolution

Hydrogen and methane contribute to about 95% of the gas yield during radiolysis of polyisobutylene. The rest is made up of isobutylene and other mostly unidentified fragments.[175–179] It was found that the ratio of methane to hydrogen remains constant over a wide range of doses, whereas the ratio of isobutylene to hydrogen or methane rises rapidly with dose.[175,176] Moreover, it has been reported that the gas yields are largely independent of irradiation temperature.[180]

#### 5.5.2.3.2 Changes in Microstructure

The main processes observed and reported are formation of vinylidene double bonds[175,176,181] and abstraction of methyl groups. The concentration of unsaturations located mainly at the end of a polymer chain produced during radiolysis was found to be increasing with dose.[180] Moreover, a linear relationship between unsaturations and scissions formed was noted over the temperature range of 83 to 363 K (–310 to 194°F). The ratio of double bonds to scissions was found to be independent of temperature and dose.[175,176,178]

#### 5.5.2.3.3 Degradation and Cross-Linking

Degradation is the predominant process in irradiation of polyisobutylene. Generally, the scission yield increases with temperature in accord with the temperature dependence of the formation of unsaturation.[182] For

poly(isobutylene-isoprene), it was found that the rate of degradation decreased with the increased content of isoprene in the copolymer, in accord with peroxide studies.[183] An extrapolation of this function to higher concentrations of unsaturation indicated that net cross-linking is expected to occur above approximately 5 mol% isoprene. A drastically different response to radiation was found for chlorinated poly(isobutylene-isoprene), poly(isobutylene-isoprene-divinylbenzene) terpolymers,[153] and dehydrohalogenated chlorobutyl rubber.[184] Rapid gelation occurred in those polymers already at low doses. The gradual depletion of these reactive sites by cross-linking then leads to prevailing degradation.[185] Certain additives can affect the response of these elastomers to irradiation. Polymercaptane compounds retard the net degradation of polyisobutylene and cause rapid gelation of poly(isobutylene-isoprene) and chlorobutyl rubber.[153,160,161] Allyl acrylate was found to cause gelation of polyisobutylene.[186]

### 5.5.2.3.4  Physical Properties

It is possible to cross-link polyisobutylene and poly(isobutylene-isoprene) and chlorobutyl rubber by means of certain additives; however, the physical properties of the vulcanizates prepared by conventional curing methods cannot be attained. The most promising results were obtained with chlorobutyl compounds containing thioether polythiols as prorads.[161]

### 5.5.2.4  Ethylene-Propylene Copolymers and Terpolymers

Commercial grades of ethylene-propylene copolymers (EPR) contain 60–75 mol% of ethylene to minimize crystallization. The addition of a third monomer, such as 1,4-hexadiene, dicyclopentadiene, or 5-ethylidene-2-norbornene, produces generally amorphous faster-curing elastomers. A large number of such terpolymers, referred to as EPDM, is available commercially. Their properties, performance, and response to radiation vary considerably depending on macrostructure, ethylene/propylene ratio, as well as on the type, amount, and distribution of the third monomer.

When EPDM is irradiated, the nature of the radical formed depends on the third monomer used[187,188] and, as in most cases, the radical concentration increases linearly with dose.[189]

### 5.5.2.4.1  Cross-Linking

The cross-linking rate of EPR by radiation comes close to that of polypropylene. EPDM terpolymers exhibit an enhanced cross-linking rate, and it increases with the diene content. However, not only the cross-linking rate, but also a greater yield of scissions results from the addition of the third monomer.[190]

Cross-linking of EPR can be promoted by the addition of a variety of additives, particularly by those that were found effective in polypropylene. Tetravinyl silane, chlorobenzene, nitrous oxide, allyl acrylate, neopentyl chloride,[191,192] and N-phenyl maleimide[193] were reported to promote the process.

*5.5.2.4.2 Physical Properties*

Radiation cured carbon-black-filled EPDM compounds exhibit tensile strength comparable to that of their analogues vulcanized by sulfur-accelerator systems.[194] Similar results were obtained from compounds containing up to 20 phr of acrylic additives, such as trimethylolpropane trimethacrylate, ethylene glycol dimethacrylate, triallyl phosphite, triallyl cyanurate, and others.[194] It should be noted, however, that some of the resulting compounds may be composed of two more or less independent, at least partially, separated networks. The noted lower compression set and reduced swelling in oils of the radiation cured samples are most likely the result of this different morphology.[195] Among the variety of EPDM grades, those containing ethylidene norbornene exhibit the fastest rate of radiation cross-linking.[193,195,196]

Extender oils were found to cause a considerable increase in the dose required to attain the optimum cure. This can be explained by reaction of transient intermediates formed on the irradiated polymer chain with the oil and with the energy transfer, which is particularly effective when the oil contains aromatic groups. Thus, the ranking of oils as to their cure inhibition is aromatic > naphtenic > aliphatic.[195] This aspect is very important because many carbon-black-reinforced EPDM compounds contain frequently 100 phr or more oil.

### 5.5.2.5 Polychloroprene

Polychloroprene is the polymer of 2-chloro-1,3 butadiene. Emulsion polymerization produces an almost entirely *trans*-1,4 polymer, which is highly crystalline. Less crystalline polychloroprenes are produced by incorporating several wt.% of 2,3-dichloro-1,3 butadiene into the polymer to break up crystalline sequences.

Irradiation of carbon-black-reinforced polychloroprene compounds produced a maximum tensile strength of 20 MPa (2,900 psi) at a dose of 20 Mrad (200 kGy), which is a value obtained typically from chemically cured compounds. The addition of 20 phr of *N,N'*-hexamethylene-bis methacrylamide as a prorad in the above compound produced a tensile strength of 18 MPa (2,610 psi) at a dose of 7 Mrad (70 kGy). Further addition of 6 phr of hexachloroethane caused the deterioration of the tensile strength by 50% at the 7 Mrad (70 kGy) dose.[197]

When irradiating a 1:1 blend of polychloroprene and poly(butadiene-acrylonitrile) (NBR) reinforced by 50 phr furnace black and containing 5–15 phr of tetramethacrylate of bisglycerol phtalate, the product exhibited a tensile strength of 20 MPa (2,900 psi) at a dose of 15 Mrad (150 kGy) with values of elongation at break in the range of 420–480%. These values are equal to or better than those obtained from similar compounds cured chemically.[198]

Irradiation of polychloroprene latexes of two different structures, one containing some sulfur and having a lower degree of branching and the other a highly branched polymer, made by mercaptane modification, showed a

more rapid cross-linking of the branched polymer. The presence of the latex dispersion medium further enhanced the cross-linking process. The concentration of free radicals in the irradiated latexes was about 50% higher than that in the coagulated and subsequently dried rubber films.[199]

Polyorthoaminophenol (2 wt.%) and polyorthoaminophenol + phenyl-β-naphtylamine (0.7 wt.% each) acted as antirads, preventing any significant cross-linking on exposure to 24 krad (240 Gy).[200,201] The addition of a diphenylamine derivative gave reasonable protection to radiation up to 22 Mrad (220 kGy).[201]

### 5.5.2.6  Silicone Elastomers

There are a large variety of elastomers based on a chain –Si–O–Si–, with different groups attached to the Si atom, that affect the properties of the polymer. Technologically, the most widely used silicone elastomers are those with all methyls on the silicone atoms, i.e., polydimethylsiloxanes (PDMSs), or ones with less than 0.5 mol% of vinyl substitution for the methyls.[202]

Irradiation of PDMS produces hydrogen, methane, and ethane. The gas yield at room temperature correlates with the concentration of cross-links formed.[203] This can be expected since double bonds cannot be formed.

#### 5.5.2.6.1  Cross-Linking

Cross-linking is a predominant process during irradiation of siloxane polymers. Chain scissions are negligible.[204–206] The cross-link density increases linearly with a dose up to 160 Mrad (1,600 kGy).[207] At 5.0 MGy (500 Mrad) the G(X) value is 0.5.[208] Free radical scavengers, such as *n*-butyl and *tert*-dodecyl mercaptan and diethyl disulfide, are the most effective antirads.[209,210] At a concentration of 10%, two-thirds of the cross-links were prevented from forming; however, the scission yield was also increased.

#### 5.5.2.6.2  Physical Properties

The tensile strength of polydimethylsiloxane irradiated by a dose of 60 kGy (6 Mrad) is 15% lower than that of PDMS cross-linked by peroxide, but when 0.14 mol% of vinyl unsaturation is substituted for the methyl groups, the tensile strength is 30% higher.[208] Irradiation of PDMS containing 55 phr silica filler by a dose of 40 kGy exhibited a superior abrasion resistance when compared to peroxide vulcanizates even after prolonged thermo-oxidative aging at 523 K (482°F). The tensile properties of the materials prepared by both of these cross-linking methods were similar. An optimum tensile strength of 8 MPa (1,160 psi) was obtained on exposure to 4 Mrad (40 kGy).[208]

### 5.5.2.7  Fluorocarbon Elastomers

Fluorocarbon elastomers represent the largest group of fluoroelastomers. They have carbon-to-carbon linkages in the polymer backbone and a varied

amount of fluorine in the molecule. In general, they may consist of several types of monomers: polyvinylidene fluoride (VDF), hexafluoropropylene (HFP), trifluorochloroethylene (CTFE), polytetrafluoroethylene (TFE), perfluoromethylvinyl ether (PMVE), ethylene, or propylene.[211] Other types may contain other co-monomers, e.g., 1,2,3,3,3-pentafluoropropylene instead of HFP.[212] Fluorocarbon elastomers exhibit good chemical and thermal stability and good resistance to oxidation.

Since fluorocarbon elastomers being discussed here contain hydrogen in their molecules, they have the tendency to cross-link in addition to scission, common in fluoropolymers when exposed to radiation. The cross-linking predominates, but there is still a significant degree of chain scission.[213]

The use of cross-linking promoters (prorads), such as diallyl maleate, triallyl cyanurate (TAC), triallyl isocyanurate (TAIC), trimethylolpropane methacrylate (TMPTM), and *N,N′*-(*m*-phenylene)-bismaleimide (MPBM) at amounts up to 10 wt.%, reduces the dose needed and the damage to the elastomeric chain by the radiation. It appears that individual fluorocarbon elastomers have the best cross-link yield with a specific prorad.[214–216] For example, copolymers of vinylidene fluoride (VDF) and hexafluoropropylene (CTFE) (e.g., Viton® A) and copolymers of vinylidene fluoride and chlorotrifluorethylene (Kel-F®) attain a high gel content and thermal stability up to 473 K (392°F) when cross-linked with a dose as low as 10–15 kGy without prorads, and only 2 kGy with 10 phr of multifunctional acrylates. Such thermal stability is unattainable with conventional chemical curing. Mechanical properties (tear resistance, tensile strength) are better than those from vulcanizates prepared by peroxide cross-linking.[217] The VDF-HFP copolymer is cross-linked by electron beam more efficiently than the copolymer of VDF and CTFE.[218]

Perfluoroelastomers (ASTM designation FFKM) are copolymers of two perfluorinated monomers, such as TFE and PMVE, with a cure site monomer (CSM), which is essential for cross-linking. Certain FFKMs can be cross-linked by ionizing radiation.[219] The advantage of radiation cured FFKM is the absence of any additives, so that the product is very pure. The disadvantage is the relatively low upper-use temperature of the cured material, typically 150°C, which limits the material to special sealing applications only.[220]

### 5.5.2.8 Fluorosilicone Elastomers

Fluorosilicone elastomers generally respond to ionizing radiation in a fashion similar to that of silicone elastomers (polydimethylsiloxanes). One interesting application is a process of preparing blends of fluoroplastics, such as poly(vinylidene fluoride), with fluorosilicone elastomers to obtain materials having a unique combination of flexibility at low temperatures and high mechanical strength.[221]

Efficiencies of radiation-induced reactions of selected elastomers are in Table 5.7. Tensile strength data from another group are in Table 5.8.

**TABLE 5.7**

Efficiencies of Radiation-Induced Elastomer Reactions

| Polymer | G(X) | G(H$_2$)[a] | G(S)/G(X)[a] |
|---|---|---|---|
| Polyisoprene (natural rubber) | 0.9 | 0.43–0.67[b] | 0.16 |
| | | 0.25–0.3[c] | |
| Polybutadiene | 3.6 | 0.23[d] | 0.1–0.2 |
| Styrene-butadiene copolymer with 60 mol% styrene | 0.6 | 0.11[d] | — |
| Styrene-butadiene copolymer with 23.4 mol% styrene | 1.8–3.8 | 0.45 (87% H$_2$) | 0.2–0.5 |
| Ethylene-propylene rubber | 0.26–0.5 | 3.3 | 0.36–0.54 |
| | | | G(S) = 0.3–0.46 |
| EPDM (with dicyclopentadiene co-monomer) | 0.91 | — | G(S) = 0.29 |
| Polyisobutylene | 0.05 | 1.3–1.6 | G(S) = 1.5–5 |
| Copolymer of vinylidene fluoride and hexafluoropropylene | 1.7 | 0.27 | G(S) = 1.36 |
| | | G(HF) = 1.2 | |
| Copolymer of vinylidene fluoride and chlorotrifluoroethylene | 1.03 | — | G(S) = 1.56 |

[a]  Unless otherwise stated.
[b]  For doses up to 2 MGy (200 Mrad).
[c]  Polyisoprenes with high 1,2 and 3,4 content.
[d]  For a mixture of H$_2$ and CH$_4$.

### 5.5.2.9 *Thermoplastic Elastomers*

Thermoplastic elastomers (TPEs) are either block copolymers (SBS, SEBS, SEPS, TPU, COPA, COPE) or blends, such as TPO (elastomer/hard thermoplastic, also referred to as thermoplastic olefin) and TPV (thermoplastic vulcanizate, blend of a vulcanized elastomer and a hard thermoplastic). These types represent the majority of the TPEs; other types are either specialty or small-volume materials.

Normally, TPEs are not cross-linked because the thermoplastic nature is their desired property in most cases. However, in some cases cross-linking is used to improve mechanical properties, influence flow[222] to reduce swelling in oils and solvents, eliminate dissolution of the polymer in oils and solvents, increase heat resistance, and influence other performance characteristics. Examples where cross-linking by ionizing radiation is necessary for the given processes are:

- Wire and cable insulation (to improve resistance to abrasion and cut-through)
- Thermoplastic foams (partial cross-linking of the material by EB increases the melt strength)
- Heat-shrinkable films, sheets, and tubing

**TABLE 5.8**

Tensile Strength Data from Selected EB-Irradiated Elastomers

| Polymer | Additive | Amount of Additive, phr | Dose, kGy | Tensile Strength, MPa (psi) |
|---|---|---|---|---|
| Natural rubber | o-Dichlorobenzene | 3 | 140 | 9 (1,305) |
| | Mono- and multifunctional acrylates | 5–20 | 140 | 15–18 (2,175–2,610) |
| | Carbon black | 50–60 | 1,000 | 1.6 (232) |
| | No additives | — | 600 | 4.8 (696) |
| Polybutadiene | Carbon black and dichlorobenzene | 50 2 | 8,000 | 15.2 (2204) |
| Copolymer of butadiene and styrene (23.5 mol% styrene) | Carbon black | 50 | 28,000 | 20.4 (2,958) |
| NBR (copolymer of butadiene and acrylonitrile) (32 mol% acrylonitrile) | Carbon black | 50 | 10,000 | 22 (3,190) |
| Polychloroprene | Carbon black | NA | 20,000 | 20 (2,900) |
| | Carbon black and diacrylamide | 20 NA | 700 | 18 (2,610) |
| Blend of polychloroprene and NBR | Carbon black and multifunctional acrylate | 50 5–15 | 15,000 | 20 (2,900) |

Thermoplastic elastomers based on polyolefins (TPO) are blends of PE or PP with EPDM elastomers wherein the elastomer is often cross-linked using thermochemical systems.[223] TPOs more suitable for medical products with no chemical residuals can be made using EB processing to cross-link the elastomer portion in such an elastomer-plastic blend. The thermoplastic governs the melt transition, and thus the extrusion properties of TPOs. The radiation response of these materials is also governed by the choice of the thermoplastic. An example of an EB cured blend of EPDM and polyethylene used is for fluid transmission tubing and electrical insulation.[224]

A review article on electron beam processing of elastomers was written by Drobny.[225]

## 5.6  Electron Beam Processing of Liquid Systems

Electron beam processing of solvent-free liquid systems for coatings, inks, and paints involves essentially polymerization and cross-linking using electrons with energies between 120 and 300 keV. Initiation by electrons leads primarily to free radical reactions. Cationic polymerization is only found in rare cases.[226–230]

Typical liquid systems require doses between 10 and 50 kGy. They consist of binders (prepolymers) with acrylic ($H_2C=CH–CO–O–$) double bonds in the main chain (polymaleates and polyfumarates) and of monomers, usually acrylates used as reactive thinners.[230] Other ingredients added to the formulation may be pigments, dyes, fillers, flatting agents, and additives to improve film and surface properties and attain the required performance criteria.[231]

Reactive prepolymers used as binders are produced by acrylation of oligomers, such as epoxy resins, urethanes, polyesters, silicones, oligo-butadiene, melamine derivatives, cellulose, and starches.[232–234] Prepolymers are the principal ingredients of coating formulations and largely determine the basic properties of the coating. Examples of industrially important acrylated prepolymers are in Table 5.9.

Monomers, also called reactive thinners, are used to reduce the viscosity of the prepolymers, but also have an effect on properties of the cured film. They form a high-molecular-weight network with the prepolymer after curing. In order to attain an adequate degree of cross-linking, principally bifunctional and polyfunctional acrylates are used. Monofunctional acrylates give a less reactive coating and are less desirable ingredients because of their volatility, odor, and skin-irritating effects. Currently, the following bifunctional and polyfunctional acrylates are used in industrial applications:

Tripropylene glycol diacrylate (TPGDA)
1,6-Hexanediol diacrylate (HDDA)
Dipropylene glycol diacrylate (DPGDA)

**TABLE 5.9**

Examples of Acrylate Prepolymers Used for Radiation Technology

$$CH_2=CH-\overset{\overset{\displaystyle O}{\|}}{C}-O-(CH_2)_6-[O-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-O-(CH_2)_6-]-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH=CH_2$$

**Polyester acrylate**

$$H_2C=HC-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2\overset{\overset{\displaystyle OH}{|}}{CH}-R-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2O-CH=CH_2$$
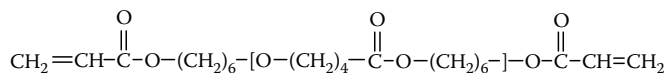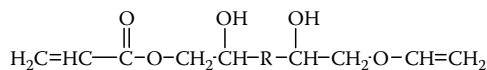
R = Bisphenol A

**Epoxy acrylate**

$$CH_2=CH-\overset{\overset{\displaystyle O}{\|}}{C}-O-(CH_2)_6-O-\overset{\overset{\displaystyle O}{\|}}{\underset{}{C}}-\overset{\overset{\displaystyle H}{|}}{N}-R-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-O-(CH_2)_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH=CH_2$$

R =

or

or   OCN—(CH₂)₆-NCO

**Polyurethane acrylate**

$$CH_2=CH-\overset{\overset{\displaystyle O}{\|}}{C}-O-R-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-[O-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-]_n O-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-R'-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH=CH_2$$

R, R' =  —CH₂-$\overset{\overset{\displaystyle }{|}}{C}$=CH₂  or  —CH₂- CH=CH—
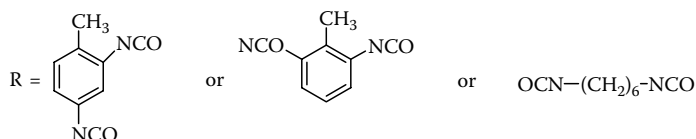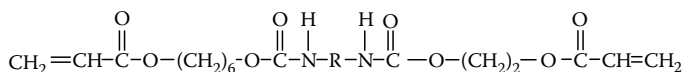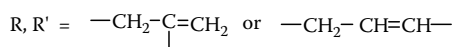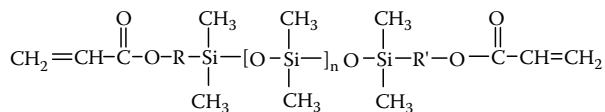
**Silicone acrylate**

Trimethylolpropane triacrylate (TMPTA)

Trimethylolpropane ethoxytriacrylate (TMP(EO)TA)

Trimethylpropane propoxytriacrylate (TMP(PO)TA)

Pentaterythritol triacrylate (PETA)

Glyceryl propoxytriacrylate (GPTA)

Ethoxylated and propoxylated acrylates are highly reactive, yet exhibit less skin irritation.[229]

Electron beam curing of coatings requires an inert atmosphere to prevent oxygen inhibition. Inertization is done by nitrogen, obtained by vaporization of liquid nitrogen. Another advantage of using an inert atmosphere is to prevent formation of ozone, which is formed in the presence of air. Often part of the gas is used for convective cooling of the accelerator beam window.

Many of the liquid systems curable by electron beam equipment are very similar to those cured by UV radiation. The EB process has the advantage that it offers the possibility of curing much thicker coats and pigmented formulations at much higher speeds than UV radiation. There is no need to use photoinitiator systems, which are often expensive and sometimes discolor the finished film. EB cured coatings have frequently better adhesion to substrate because of the penetration of the electrons. These advantages are offset by the much higher capital cost of the EB equipment.[235] Another issue is to have enough production to sufficiently utilize the highly productive electron beam equipment. In some cases to combine UV and EB processes is of technological or economical advantage.

## 5.7 Grafting and Other Polymer Modifications

### 5.7.1 Grafting

Radiation-induced grafting in its simplest form involves heterogeneous systems, with the substrate being film, fiber, or even powder and the monomer to be grafted onto the substrate a neat liquid, vapor, or solution.[236–241] Currently, three main radiation grafting techniques are known:[237,242]

1. The pre-radiation procedure
2. The peroxidation procedure
3. Simultaneous method

In the *pre-radiation procedure*, the substrate is first irradiated, usually *in vacuo* or inert gas, to produce relatively stable free radicals, which are then reacted with a monomer, usually at elevated temperatures. A major advantage is minimization of homopolymer formation.[246]

The *peroxidation procedure*, which is the least often used of all the irradiation techniques, involves irradiation of the substrate in the presence of air or oxygen. This produces diperoxides and hydroperoxides on the surface of the substrate, which are stable, and the substrate can be stored until the combination with a monomer is possible. Monomer, with or without solvent, is then reacted with the activated peroxy trunk polymer in air or under vacuum at elevated temperatures to form the graft copolymer. The advantage of this method is the relatively long shelf life of the intermediate peroxy trunk polymers before the final grafting step.[243]

In the *simultaneous method*, which is the one most commonly used, the substrate is irradiated while in direct contact with the monomer. The monomer can be present as a vapor, liquid, or solution. This grafting process can occur via free radial or ionic mechanism.[244,245] With the simultaneous method, the formation of homopolymer is unavoidable, but there are several systems to minimize it. The advantage of this method is that both monomer and substrate are exposed to the radiation source and both form reactive sites. The other two techniques rely upon rupture of the bond to form reactive sites, and therefore require higher radiation doses. Thus, the simultaneous method is more suitable for substrates sensitive to radiation. The simultaneous method can utilize UV radiation besides EB source. Logically, the UV irradiation requires a photoinitiator or sensitizer to achieve an acceptable level of grafting.

Radiation grafting can be performed with the monomers being neat or dissolved. In some cases the use of solvents can produce graft copolymers with unique properties. Solvents, which wet and swell the backbone polymers, often assist grafting. Certain additives, including mineral acids and inorganic salts, such as lithium perchlorate, as well as monomers, such as divinyl benzene (DVB) and trimethylolpropane triacrylate (TMPTA), improve grafting yields.[242,246]

The dose rate affects both the yield and chain length of the grafted material. Air has a detrimental effect on grafting since it inhibits the reaction, which is consistent with other radiation-induced free radical reactions. Increasing the temperature of the grafting system increases the yield. This is very likely because raising the temperature increases the diffusion rate of the monomer into the substrate.[245]

Theoretically, radiation grafting is applicable to any organic backbone polymer. PVC grafting yields are among the highest under the radiation grafting conditions. Acid enhancement is observed for most backbone polymers. Solvent effects are also relevant to many backbone polymer systems (see Table 5.10). At low styrene solution concentrations (e.g., 30%) a peak in grafting is observed. This, the *Trommsdorff peak*,[247] is important since the chain length of graft is a maximum under these conditions and the graft yield reaches a maximum.

Substituents have an effect as in conventional polymerization reactions. In radiation grafting certain substituents activate monomers, and others deactivate them.[248,249] These effects can be seen in Table 5.11.

**TABLE 5.10**

Effect of Solvents on Radiation Grafting of Styrene to Polypropylene[a]

| | Grafting Yield, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Styrene (wt.% in Solution) | | | | | | | |
| Solvent | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 100 |
| Methanol | 29 | 94 | 50 | 37 | 36 | 35 | 29 | 22 |
| Ethanol | 44 | 89 | 65 | 47 | 36 | 32 | 30 | 22 |
| *n*-Butanol | 123 | 74 | 34 | 40 | 33 | 29 | 28 | 22 |
| *n*-Octanol | 49 | 107 | 68 | 42 | 32 | 29 | 26 | 22 |
| Dimethylformamide | 24 | 40 | 43 | 44 | 40 | 39 | 33 | 22 |
| Dimethylsulfoxide | 11 | 29 | 66 | 61 | 56 | 42 | 24 | 21 |
| Acetone | 13 | 20 | 24 | 25 | 22 | 24 | 25 | 22 |
| 1,4-Dioxane | 6 | 12 | 15 | 17 | 19 | 21 | 23 | 22 |

[a]  Total dose, 3 kGy; dose rate, 0.4 kGy/h.
*Source:*  Dworjanin, P., and Garnett, J. L., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Publishers, p. 30 (1992). With permission of Carl Hanser Publishers.

Multifunctional monomers, such as acrylates (e.g., TMPTA), were found to have a dual function: to enhance the copolymerization and to cross-link the grafted trunk polymer chains. An addition of an acid along with a polyfunctional monomer has synergistic effects on grafting.[250]

Although many radiation-grafted materials have been discovered, only a limited number of them have been commercially utilized.[251,252] One of the first successful applications was the use of grafted films in battery separators.[253] Other possibilities are in ion exchange resins and membranes for separation processes.[254] The textile industry represents opportunities in improving

**TABLE 5.11**

Radiation Grafting of Miscellaneous Monomers[a] onto Cellulose

| Monomer | Grafting Yield, % |
|---|---|
| Styrene[b] | 40 |
| *o*-Methylstyrene[b] | 110 |
| *p*-Methylstyrene[b] | 6 |
| *o*-Chlorostyrene[b] | 74 |
| 2-Vinyl pyridine[b] | 3 |
| Methyl methacrylate[c] | 18 |
| Vinylacetate[d] | 11 |

[a]  40 vol.% in methanol.
[b]  Total dose, 5.4 kGy; dose rate, 0.45 kGy/h.
[c]  Total dose, 10 kGy; dose rate, 0.45 kGy/h.
[d]  Total dose, 10 kGy; dose rate, 3.9 kGy/h.

flame retardation, permanent press, dyeing, and antistatic properties.[255,256] Other processes based on radiation grafting are useful in medicine (diagnostic and therapeutic) and industry (fermentation, bioseparation) and for producing catalyst supports.[257]

*Radiation rapid curing* (RRC) is another promising application of radiation grafting.[254] It is used for films containing oligomer-monomer mixtures, which cross-link within a fraction of a second when exposed to electrons from low-energy EB equipment.[258,259] In this process multifunctional acrylates are used and have a dual function: they accelerate the rate of polymerization and also cross-link the film. The greatest potential is in packaging and in plastics industries for coating and ink applications.[257]

### 5.7.2 Other Polymer Modifications

Other polymer modifications involve surface or bulk modifications, and a majority of them are used in medical technology. Examples of these processes are:

- Modifications of surface of materials adapted for contact with human or animal tissues to impart biofunctional properties. These apply typically to ocular implants, surgical instruments, medical devices, or contact lenses.[260]
- Enhancing the wear resistance of polymers (e.g., ultra-high-molecular-weight polyethylene–UHMWPE–used for *in vivo* implants, such as artificial hip joints).[261]
- Electron beam cross-linking of hydrogels based on synthetic polyethylene oxide to produce materials for corneal prostheses.[262]
- Producing polyethylene microporous film with a porosity of 20 to 80% for battery separators.[263]
- Three-dimensional processing of materials by electron beam to produce uniform isotropic irradiation of components, which are to be sterilized or bulk/surface modified.[264]

A comprehensive review of radiation techniques in the formulation of biomaterials was published by Kaetsu.[265] Substrate modification by electron beam was discussed by Wendrinski at the meeting of RadTech Europe 2001.[266]

## References

1. Kase, K. R., and Nelson, W. R., *Concepts of Radiation Chemistry*, Pergamon Press, New York (1978).
2. Davidson, R. S., *Exploring the Science, Technology and Applications of U.V. and E.B. Curing*, SITA Technology, London, p. 123 (1999).

3. Lowe, C., in *Chemistry and Technology of U.V. and E.B. Formulations for Coatings, Inks and Paintings*, Vol. 4 (Oldring, P. K. T., Ed.), SITA Press, London, Chapter 1 (1991); Lowe, C., and Oldring, P. K. T., in *Chemistry and Technology of U.V. and E.B. Formulations for Coatings, Inks and Paintings*, Vol. 4 (Oldring, P. K. T., Ed.), SITA Press, London, Chapter 2 (1991).

4. Schafer, O. et al., *Photochem. Photobiol.*, 50, p. 717 (1989).

5. *Irradiation Effects on Polymers* (Clegg, D. W., and Collier, A. A., Eds.), Elsevier, London (1991).

6. *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser Publishers, Munich (1992).

7. Mehnert, R., in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A22 (Elvers, B., Hawkins, S., Russey, W., and Schulz, G., Eds.), VCH, Weinheim, p. 471 (1993).

8. Garratt, P., *Strahlenhärtung*, Curt Vincentz Verlag, Hannover, p. 41 (1996). In German.

9. Tabata, T., and Ito, R., *Nucl. Sci. Eng.*, 53, p. 226 (1976).

10. Frankewich, E. L., *Usp. Khim.*, 35, p. 1161 (1966).

11. Hirsch, J., and Martin, E., *Solid State Commun.*, 7, pp. 279 and 783 (1969).

12. Dole, M., Böhm, G. G. A., and Waterman, D. C., *Polym. J. Suppl.*, 5, p. 93 (1969).

13. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Technology and Equipment*, Vol. 1, John Wiley & Sons, Chichster/SITA Technology Ltd., London, p. 24 (1998).

14. Buijsen, P., *Electron Beam Induced Cationic Polymerization with Onium Salts* (Thesis, Delft University of Technology), Delft University Press (1996).

15. von Raven, A., and Heusinger, H., *J. Polym. Sci.*, 12, p. 2235 (1974).

16. Kaufmann, R., and Heusinger, H., *Makromol. Chem.*, 177, p. 871 (1976).

17. Katzer, H., and Heusinger, H., *Makromol. Chem.*, 163, p. 195 (1973).

18. Zott, H., and Heusinger, H., *Makromolekules*, 8, p. 182 (1975).

19. Kuzminskii, A. S., and Bolshakova, S. I., *Symp. Rad. Chem. 3rd*, Tihany, Hungary (1971).

20. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 592 (1982).

21. Tabata, T., and Ito, R., *Nucl. Sci. Eng.*, 53, p. 226 (1976).

22. Garratt, P., *Strahlenhärtung*, Curt Vincentz Verlag, Hannover, p. 42 (1996). In German.

23. Miller, A. A., Lawton, E. J., and Balwit, J. S., *J. Polym. Sci.*, 14, p. 503 (1954).

24. Charlesby, A., *Atomic Radiation and Polymers*, Pergamon, Oxford (1960).

25. Wall, L. A., *J. Polym. Sci.*, 17, p. 141 (1955).

26. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 583 (1982).

27. Charlesby, A., and Pinner, S. H., *Proc. R. Soc. London Ser.*, A249, p. 367 (1959).

28. Clough, R., in *Encyclopedia of Polymer Science and Engineering*, Vol. 13 (Kroschwitz, J. I., Ed.), John Wiley & Sons, New York, p. 673 (1988).

29. Pearson, R. W., Bennett, J. V., and Mills, I. G., *Chem. Ind. (London)*, p. 1572 (1960).

30. Kozlov, V. T., Yevseyev, A. G., and Zubov, P. I., *Vysokomol. Soed.*, A11, p. 2230 (1969).

31. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 583 (1982).

32. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 593 (1982).

33. Chapiro, A. J., *Chim. Phys.*, 47, pp. 747 and 764 (1950).

34. Dogadkin, B. A., et al., *Vysokomol. Soedin.*, 2, p. 259 (1960).

35. Jankowski, B., and Kroh, J., *J. Appl. Polym. Sci.*, 13, p. 1795 (1969).

36. Jankowski, B., and Kroh, J., *J. Appl. Polym. Sci.*, 9, p. 1363 (1965).

37. Kozlov, V. T., et al., *Vysokomol. Soedin.*, A10, p. 987 (1968).

38. Kozlov, V. T., Klauzen, N. A., and Tarasova, Z. N., *Vysokomol. Soedin.*, A10, p. 1949 (1968).
39. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 593 (1982).
40. Nikolskii, V. G., Tochin, V. A., and Buben, N. Ya., Elementary Process of High Energy, *Izd. Nauka* (1965). In Russian.
41. Turner, D., *J. Polym. Sci.*, 27, p. 503 (1958).
42. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 596 (1982).
43. Okada, Y., *Adv. Chem. Ser.*, 66, p. 44 (1967).
44. Karpov, V. I., *Vysokomol. Soedin.*, 7, p. 1319 (1965).
45. Scholes, G., and Sinic, M., *Nature*, 202, p. 895 (1964).
46. Lyons, B. J., and Dole, M., *J. Phys. Chem.*, 68, p. 526 (1964).
47. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 596 (1982).
48. Geymer, D. O., and Wagner, C. D., *Polym. Prep. Am. Chem. Soc. Div. Polym. Chem.*, 9, p. 235 (1968).
49. Kaurkova, G. K., Kachan, A. A., and Chervyntsova, L. L., *Vysokomol. Soedin.*, 7, p. 183 (1965); *J. Polym. Sci. Part C*, 16, p. 3041 (1967).
50. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 597 (1982).
51. Geymer, D., *Macromol. Chem.*, 100, p. 186 (1967).
52. Geymer, D. O., and Wagner, C. D., *Polym. Prep. Am. Chem. Soc. Div. Polym. Chem.*, 9, p. 235 (1968).
53. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 600 (1982).
54. Miller, S. M., Roberts, R., and Vale, L. R., *J. Polym. Sci.*, 58, p. 737 (1962).
55. Miller, S. M., Spindler, M. W., and Vale, L. R., in *Proc. IAEA Conf. Appl. Large Rad. Sources Ind.*, Salzburg, Vol. 1, p. 329 (1963).
56. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 601 (1982).
57. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 601 (1982).
58. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 603 (1982).
59. Pearson, D. S., and Shurpik, A., U.S. Patent 3,848,502 to Firestone Tire and Rubber (1974).
60. Zapp, R. L., and Oswald, A. A., Paper 55, Meeting of the Rubber Division of the American Chemical Society, Cleveland (1975).
61. Griesbaum, K., *Angew. Chem. Ind. Ed. Engl.*, 9, p. 273 (1970).
62. Morgan, C. R., Magnotta, F., and Kelley, A. D., *J. Polym. Sci. Polym. Chem.*, 15, p. 627.
63. Morgan, C. R., and Kelley, A. D., *J. Polym. Sci. Polym. Lett.*, 16, p. 75 (1978).
64. Pierson, R. M., et al., *Rubber Plast. Age*, 38, pp. 592, 708, and 721 (1957).
65. Walling, C., and Helmreich, W., *J. Am. Chem. Soc.*, 81, p. 1144 (1978).
66. Böhm, G. G. A., *The Radiation Chemistry of Macromolecules*, Vol. II (Dole, M., Ed.), Academic Press, New York, Chapter 12 (1972).
67. Miller, A. A., *Ind. Eng. Chem.*, 51, p. 1271 (1959).
68. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 604 (1982).
69. Smith, W. V., and Simpson, V. G., U.S. Patent 3,084,115 to U.S. Rubber Co. (1963).
70. Lyons, B. J., *Nature*, 185, p. 604 (1960).
71. Odian, G., and Bernstein, B. S., *Nucleonics*, 21, p. 80 (1963).
72. Geymer, D. O., and Wagner, C. D., *Polym. Prep. Am. Chem. Soc.*, 9, p. 235 (1968).
73. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 606 (1982).
74. Turner, D., *J. Polym. Sci.*, 27, p. 503 (1958).
75. Blanchford, J., and Robertson, P. F., *J. Polym. Sci.*, 3, pp. 1289, 1303, 1313, and 1325 (1965).

76. Bauman, R. G., and Born, J. W., *J. Appl. Polym. Sci.*, 1, p. 351 (1959).
77. Bauman, R. G., *J. Appl. Polym. Sci.*, 2, p. 328 (1959).
78. Bradley, R., *Radiation Technology Handbook*, Marcel Dekker, New York, p. 100 (1984).
79. Bradley, R., *Radiation Technology Handbook*, Marcel Dekker, New York, p. 105 (1984).
80. Charlesby, A., *Atomic Radiation and Polymers*, Pergamon, Oxford (1960).
81. Silverman, J., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser, Munich, p. 16 (1992).
82. Silverman, J., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser, Munich, p. 17 (1992).
83. Patel, G. N., and Keller, A., *J. Polym. Sci. Phys. Ed.*, 13, p. 305 (1975).
84. Chappas, W. J., and Silverman, J., *Radiat. Phys. Chem.*, 16, p. 437 (1980).
85. Liu, Z., Markovic, V., and Silverman, J., *Radiat. Phys. Chem.*, 25, p. 367 (1985).
86. Luo, Y., et al., *Radiat. Phys. Chem.*, 25, p. 359 (1985).
87. Lyons, B. J., *Radiat. Phys. Chem.*, 28, p. 149 (1986).
88. Zoepfl, F. J., Markovic, V., and Silverman, J., *J. Polym. Sci. Chem. Ed.*, 22, p. 2017 (1984).
89. Kashiwabara, H., and Seguchi, T., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser, Munich, Chapter 11 (1992).
90. Silverman, J., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser, Munich, p. 18 (1992).
91. Silverman, J., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser, Munich, p. 19 (1992).
92. Silverman, J., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser, Munich, p. 20 (1992).
93. Barlow, A., Biggs, J. W., and Meeks, L. A., *Radiat. Phys. Chem.*, 18, p. 267 (1981).
94. Fisher, P., *The Short-Time Electric Breakdown Behavior of Polyethylene*, Annual Report, National Academy of Science Publication, Washington, DC (1982).
95. Chappas, W. J., Mier, M. A., and Silverman, J., *Radiat. Phys. Chem.*, 20, p. 323 (1982).
96. Bradley, R., *Radiation Technology Handbook*, Marcel Dekker, New York, p. 114 (1984).
97. Bradley, R., *Radiation Technology Handbook*, Marcel Dekker, New York, p. 115 (1984).
98. Bradley, R., *Radiation Technology Handbook*, Marcel Dekker, New York, p. 132 (1984).
99. McGinniss, V. D., in *Encyclopedia of Polymer Science and Engineering*, Vol. 4 (Mark, H. F., and Kroschwitz, J. I., Eds.), John Wiley & Sons, New York, p. 418 (1986).
100. Wippler, C., *J. Polym. Sci.*, 24, p. 585 (1958).
101. Clough, R. L., and Gillen, K. T., *Radiat. Phys. Chem.*, 22, p. 527 (1983).
102. Posselt, K., *Kolloid. Z. Z. Polym.*, 223, p. 104 (1958).
103. Bradley, R., *Radiation Technology Handbook*, Marcel Dekker, New York, p. 134 (1984).
104. Charlesby, A., *Atomic Radiation and Polymers*, Pergamon Press, London, p. 336 (1962).
105. Alexander, P., Charlesby, A., and Ross, M., *Proc. Roy. Soc.*, 223, p. 392 (1954).
106. McGinniss, V. D., in *Encyclopedia of Polymer Science and Engineering*, Vol. 4 (Mark, H. F., and Kroschwitz, J. I., Eds.), John Wiley & Sons, New York, p. 442 (1986).
107. Tabata, Y., *Solid State Reactions in Radiation Chemistry, Taniguchi Conference*, Sapporo, Japan, p. 118 (1992).
108. Sun, J., Zhang, Y., and Zhong, X., *Polymer*, 35, p. 2881 (1994).
109. Oshima, A., et al., *Radiat. Phys. Chem.*, 45, p. 269 (1995).
110. Lyons, B. J., in *Modern Fluoropolymers* (Scheirs, J., Ed.), John Wiley & Sons Ltd., Chichester, p. 341 (1997).

111. Korenev, S., *Radiat. Phys. Chem.*, 71, p. 521 (2004).

112. Bowers, G. H., and Lovejoy, E. R., *I&EC Product Research and Development*, 1, June, p. 89 (1962).

113. Scheirs, J., in *Modern Fluoropolymers* (Scheirs, J., Ed.), John Wiley & Sons Ltd., Chichester, p. 61 (1997).

114. Carlson, D. P., and West, N. E., U.S. Patent 3,738,923 (1973).

115. Franta, I., in *Elastomers and Rubber Compounding Materials* (Franta, I., Ed.), SNTL Prague and Elsevier, Amsterdam, p. 25 (1989).

116. Quirk, R. P., and Morton, M., in *Science and Technology of Rubber*, 2nd ed. (Mark, J. E., Burak, E., and Eirich, F. R., Eds.), Academic Press, San Diego, Chapter 2 (1994).

117. *Handbook of Elastomers*, 2nd ed. (Bhowmick, A., and Stephens, H. L., Eds.), Marcel Dekker, New York (2001).

118. Röthemeyer, F., and Sommer, F., *Kautschuktechnologie*, Carl Hanser Verlag, Munich (2001). In German.

119. White, J. L., *Rubber Processing*, Hanser Publishers, Munich (1995).

120. Hamed, G., in *Engineering with Rubber* (Gent, A. N., Ed.), Hanser Publishers, Munich, p. 20 (1992).

121. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 608 (1982).

122. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 610 (1982).

123. Flory, P. J., *Ind. Eng. Chem.*, 38, p. 417 (1946).

124. Böhm, G. G. A., et al., *J. Appl. Polym. Sci.*, 21, p. 3193 (1977).

125. Smith, T. L., in *Rheology, Theory and Application*, Vol. 5 (Eirich, F. R., Ed.), Academic Press, New York, Chapter 4 (1969).

126. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 611 (1982).

127. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 612 (1982).

128. Pearson, D. S., *Radiat. Phys. Chem.*, 18, p. 95 (1981).

129. Lal, J., *Rubber. Chem. Technol.*, 43, p. 664 (1970).

130. Kuzminskii, A., et al., in *Proceedings of the International Conference on Peaceful Uses of Atomic Energy*, Geneva, Vol. 29, p. 258 (1958).

131. Kozlov, V. T., Klauzen, N. A., and Tarasova, Z. N., *Vysokomol. Soedin.*, A10, p. 1949 (1968).

132. Kaufmann, R., and Heusinger, H., *Makromol. Chem.*, 177, p. 871 (1976).

133. Katzer, H., and Heusinger, H., *Makromol. Chem.*, 163, p. 195 (1973).

134. Turner, D., *J. Polym. Sci.*, 27, p. 503 (1958).

135. Turner, D. T., *J. Polym. Sci.*, 35, p. 541 (1960); *Polymer (London)*, 1, p. 27 (1959).

136. Mullins, L., and Turner, D. T., *Nature*, 183, p. 1547 (1959).

137. Mullins, L., and Turner, D. T., *J. Polym. Sci.*, 43, p. 35 (1960).

138. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 617 (1982).

139. Kozlov, V. T., Yevseyev, A. G., Zubov, I. P., *Vysokomol. Soedin.*, A11, p. 2230 (1969).

140. Bauman, R. G., *J. Appl. Polym. Sci.*, 2, p. 328 (1959).

141. Roberts, D. S., and Mandelkern, L., *J. Am. Chem. Soc.*, 80, p. 1289 (1958).

142. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 619 (1982).

143. Harmon, D. J., *Rubber World*, 138, p. 585 (1958).

144. Harmon, D. J., *Rubber Age*, 86, p. 251 (1959).

145. Arnold, P. M., Kraus, G., and Anderson Jr., R. H., *Rubber Chem. Technol.*, 34, p. 263 (1961).

146. Dogadkin, B. A., Mladenov, I., and Tutorskii, I. A., *Vysokomol. Soedin.*, 2, p. 259 (1960).

147. Nablo, S. V., and Makuuchi, K., *Meeting of the Rubber Division of American Chemical Society*, Pittsburg, PA, October 11–14, Paper 83 (1994).
148. Chai, C. K., et al., *Sains Malaysiana*, 37, p. 79 (2008).
149. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 620 (1982).
150. Blanchford, J., and Robertson, R. F., *J. Polym. Sci.*, 3, pp. 1289, 1303, 1313, and 1325 (1965).
151. Petrov, Ya., Karpov, V. L., and Vsesoyuz, T., *Soveshchenia po Radiatsionoi Khimii*, Academy of Science, USSR, p. 279 (1958).
152. von Raven, A., and Heusinger, H., *J. Polym. Sci.*, 12, p. 2255 (1974).
153. Böhm, G. G. A., in *The Radiation Chemistry of Macromolecules*, Vol. II (Dole, M., Ed.), Academic Press, New York.
154. Kuzminskii, A., et al., in *Proceedings of the International Conference on Peaceful Uses of Atomic Energy*, Geneva, 29, p. 258 (1958).
155. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 622 (1982).
156. Parkinson, W. W., and Sears, W. C., *Adv. Chem. Ser.*, 66, p. 37 (1967).
157. Golub, M. A., *J. Am. Chem. Soc.*, 80, p. 1794 (1958).
158. Golub, M. A., *J. Am. Chem. Soc.*, 82, p. 5093 (1960).
159. Pearson, D. S., and Shurpik, A., U.S. Patent 3,843,502 to Firestone Tire & Rubber (1974).
160. Zapp, R. L., and Oswald, A. A., Rubber Division Meeting 1975, Cleveland, American Chemical Society, Paper 55 (1975).
161. Tarasova, Z. N., et al., *Kauch. Rezina*, 5, p. 14 (1958).
162. Harmon, D. J., *Rubber Age (London)*, 84, p. 469 (1958).
163. Böhm, G. G. A., et al., *J. Appl. Polym. Sci.*, 21, p. 3139 (1977).
164. Yoshida, K., et al., *J. Macromol. Sci.*, A14, p. 739 (1980).
165. Okamoto, H., Adachi, S., and Iwai, T., *J. Macromol. Sci.*, A11, p. 1949 (1977).
166. Okamoto, H., Adachi, S., and Iwai, T., *J. Polym. Sci.*, 17, pp. 1267 and 1279 (1979).
167. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 629 (1982).
168. Dogadkin, B. A., et al., in *Proceedings of the All-Union Conference*, Riga (1960).
169. Jackson, W. W., and Hale, D., *Rubber Age*, 77, p. 865 (1955).
170. Pearson, D. S., and Böhm, G. G. A., *Rubber Chem. Technol.*, 45, p. 193 (1972).
171. Böhm, G. G. A., et al., *J. Appl. Polym. Sci.*, 21, p. 3193 (1977).
172. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 634 (1982).
173. Palalskii, B. K., et al., *Vysokomol. Soedin.*, A16, p. 2762 (1974).
174. Alexander, P., and Charlesby, A., *Proc. R. Soc. London*, A230, p. 136 (1955).
175. Alexander, P., Black, R., and Charlesby, A., *Proc. R. Soc. London*, A232, p. 31 (1955).
176. Berzkin, B. G., et al., *Vysokomol. Soedin.*, 9, p. 2566 (1967).
177. Turner, D. T., in *The Chemistry and Physics of Rubber Like Substances* (Bateman, L., Ed.), John Wiley & Sons, New York, p. 563 (1963).
178. Karpov, V. L., *Sessiya Akad. Nauk SSSR po Mirnomu Ispol. Atom. Energii*, Akad. of Sci., Moscow (1955).
179. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 635 (1982).
180. Slovokhotova, N. H., and Vsesoyuz, I. I., *Seveshchania po Radiatsionoi Khimii*, Academy of Sciences, Moscow, p. 263 (1958).
181. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 637 (1982).
182. Loan, L. D., *J. Polym. Sci.*, A2, p. 2127 (1964).
183. EXXON chemical brochure on conjugated diene butyl elastomer.
184. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 638 (1982).
185. Odian, G., and Bernstein, B. S., *J. Polym. Sci. Lett.*, 2, p. 819 (1964).

186. Geissler, W., Zott, M., and Heusinger, H., *Makromol. Chem.*, 179, p. 697 (1978).
187. Faucitano, A., Martinotti, F., and Buttafava, A., *Eur. Polym. J.*, 12, p. 467 (1969).
188. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 640 (1982).
189. Odian, G., Lamparella, D., and Canamare, J., *J. Polym. Sci.*, C16, p. 3619 (1967).
190. Geymer, D. D., and Wagner, C. D., *Polymer Prepr. Am. Chem. Soc. Div. Polym. Chem.*, 9, p. 235 (1968).
191. Smetanina, L. B., et al., *Vysokomol. Soedin.*, A12, p. 2401 (1970).
192. Pearson, D. S., and Böhm, G. G. A., *Rubber Chem. Technol.*, 45, p. 193 (1968).
193. Eldred, R. J., *Rubber Chem. Technol.*, 47, p. 924 (1974).
194. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 642 (1982).
195. Kammel, G., and Wiedenmann, R., *Siemens Forsch. Entwicklungsber.*, 5, p. 157 (1976).
196. El. Miligy, A. A., et al., *Elastomerics*, 111, p. 28 (1979).
197. Krishtal', I. V., et al., *Kauch. Rezina*, 4, p. 11 (1976).
198. Tarasova, N. N., et al., *Vysokomol. Soedin.*, A14, p. 1782 (1972).
199. Oganesyan, R. A., *Kauch. Rezina*, 1, p. 34 (1976).
200. Ito, M., Okada, S., and Kuriyama, I., *J. Mater. Sci.*, 16, p. 10 (1981).
201. Polmanteer, K. E., in *Handbook of Elastomers* (Bhowmick, A. K., and Stephens, H. L., Eds.), Marcel Dekker, New York, p. 606 (2001).
202. Ormerod, M. G., and Charlesby, A., *Polymer*, 4, p. 459 (1963).
203. Charlesby, A., *Proc. R. Soc. London Ser. A*, 230, p. 120 (1955).
204. Miller, A. A., *J. Am. Chem. Soc.*, 82, p. 3319 (1960).
205. Kilb, R. W., *J. Phys. Chem.*, 63, p. 1838 (1959).
206. Delides, C. G., and Shephard, I. W., *Radiat. Phys. Chem.*, 10, p. 379 (1977).
207. Squire, D. R., and Turner, D. T., *Macromolecules*, 5, p. 401 (1972).
208. Miller, A. A., *J. Am. Chem. Soc.*, 83, p. 31 (1961).
209. Przbyla, R. L., *Rubber Chem. Technol.*, 47, p. 285 (1974).
210. Mironov, E. I., et al., *Kauch Rezina*, 6, p. 19 (1971).
211. Drobny, J. G., *Technology of Fluoropolymers*, CRC Publishers, Boca Raton, FL, p. 93 (2009).
212. Arcella, V., and Ferro, R., in *Modern Fluoropolymers* (Scheirs, J., Ed.), John Wiley & Sons, Chichester, p. 72 (1997).
213. Böhm, G. G. A., and Tveekrem, J. O., *Rubber Chem. Technol.*, 55, p. 649 (1982).
214. Lyons, B. J., in *Modern Fluoropolymers* (Scheirs, J., Ed.), John Wiley & Sons, Chichester, p. 339 (1997).
215. Kaiser, R. J., et al., *J. Appl. Polym. Sci.*, 27, p. 957 (1982).
216. Vokal, A., et al., *Radioisotopy,* 29, p. 426 (1988), CA 112, 119976u.
217. McGinniss, V. D., in *Encyclopedia of Polymer Science and Engineering*, Vol. 4 (Mark, H. F., and Kroschwitz, J. I., Eds.), John Wiley & Sons, New York, p. 438 (1986).
218. McGinniss, V. D., in *Encyclopedia of Polymer Science and Engineering*, Vol. 4 (Mark, H. F., and Kroschwitz, J. I., Eds.), John Wiley & Sons, New York p. 439 (1986).
219. Logothetis, A. L., U.S. Patent 5,260,351 to E.I. Du Pont de Nemours and Company (November 1993).
220. Marshall, J. B., in *Modern Fluoropolymers* (Scheirs, J., Ed.), John Wiley & Sons Ltd., Chichester, UK, 1997, p. 81.
221. Caporiccio, G., and Mascia, L., U.S. Patent 5,457,158 to Dow Corning Corporation (1995).
222. Drobny, J. G., *Handbook of Thermoplastic Elastomers*, William Andrew Publishing, Norwich, N. Y. 2007, p. 150.

223. Spenadel, L., Grosser, J. H., and Dwyer, S. M., U.S. Patent 4,843,129 to Exxon Research and Engineering Company (June 1989).
224. Stine, C. R., et al., U.S. Patent 3,990,479 to Samuel Moore and Company (November 1976).
225. Drobny, J. G., *Rubber World*, Vol. 232, No. 4, July, p. 27 (2005).
226. Mehnert, R., Bögl, K. W., Helle, N., and Schreiber, G. A., in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A22 (Elvers, B., Hawkins, S., Russey, W., and Schulz, G., Eds.), VCH Verlagsgesselschaft, Weinheim, p. 479 (1993).
227. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV &EB Curing Technology & Equipment*, John Wiley & Sons, Chichester/SITA Technology Ltd., London, p. 22 (1998).
228. Janke, C. J., et al., U.S. Patent 5,877,229 to Lockheed Martin Energy Systems (1999).
229. Shu, J. S., et al., U.S. Patent 4,657,844 to Texas Instruments (1987).
230. Carroy, A. C., *Conference Proceedings of 19th Technology Days in Radiation Curing Process and Systems*, Le Mans, France, May 22–28 (1998).
231. Heger, A., *Technologie der Strahlenchemie von Polymeren*, Akademie Verlag, Berlin, 1990.
232. *Chemistry and Technology of U.V. and E.B. Formulations for Coatings, Inks and Paints* (Oldring, P. K. D., Ed.), SITA Technology Ltd., London, 1991.
233. *Radiation Curing of Polymers* (Randell, D. R., Ed.), The Royal Society of Chemistry, London, 1987.
234. *Radiation Curing of Polymeric Materials* (Hoyle, C. E., and Kinstle, J. F., Eds.), ACS Symposia Series, 417, 1990.
235. Garratt, P. G., *Strahlenhärtung*, Curt Vincentz Verlag, Hannover, p. 45 (1996). In German.
236. Charlesby, A., *Atomic Radiation and Polymers*, Pergamon Press, Oxford (1960).
237. Chapiro, A., *Radiation Chemistry of Polymeric Systems*, Wiley-Interscience, New York 1962.
238. Wellons, J. D., and Stannett, V. T., *J. Polym. Sci.*, A3, p. 847 (1965).
239. Demint, R. J., et al., *Text. Res. J.*, 32, p. 918 (1962).
240. Dilli, S., and Garrnett, J. L., *J. Appl. Polym. Sci.*, 11, p. 859 (1967).
241. Hebeish, A., and Guthrie, J. T., *The Chemistry and Technology of Cellulosic Copolymers,* Springer Verlag, Berlin, 1981.
242. Garnett, J. L., *Radiat. Phys. Chem.*, 14, p. 79 (1979).
243. Dworjanyn, P., and Garnett, J. L., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser Publishers, Munich, Chapter 6, p. 94 (1992).
244. Kabanov, V. Y., Sidorova, L. P., Spitsyn, V. I., *Eur. Polym. J.*, p. 1153 (1974).
245. Huglin, M. B., and Johnson, B. L., *J. Polym. Sci.*, A-1, 7, p. 1379 (1969).
246. Dworjanyn, P., and Garnett, J. L., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser Publishers, Munich, Chapter 6, p. 99 (1992).
247. Trommsdorf, E., Kohle, G., and Lagally, P., *Makromol. Chem.*, 1, p. 169 (1948).
248. Dilli, S., et al., *J. Polym. Sci.*, C37, p. 57 (1972).
249. Dilli, S., and Garnett, J. L., *Aust. J. Chem.*, 23, p. 1163 (1970).
250. Ang, C. H., et al., in *Biomedical Polymers, Polymeric Materials and Pharmaceuticals for Biomedical Use* (Goldberg, E. P., and Nakajima, A., Eds.), Academic Press, New York, 1960.
251. Dworjanyn, P., and Garnett, J. L., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser Publishers, Munich, Chapter 6, p. 112 (1992).
252. Stannett, V. T., Silverman, J., and Garnett, J. L., in *Comprehensive Polymer Science* (Allen, G., Ed.), Pergamon Press, New York, 1989.

253. Stannett, V. T., *Radiat. Phys. Chem.*, 35, p. 82 (1990).
254. Dworjanyn, P., and Garnett, J. L., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser Publishers, Munich, Chapter 6, p. 114 (1992).
255. Garnett, J. L., *Radiat. Phys. Chem.*, 14, p. 79 (1979).
256. Garnett, J. L., and Leeder, J. D., *ACS Symp. Ser.*, 49, p. 197 (1977).
257. Bett, S. J., and Garnett, J. L., *Proceedings of Radcure'87 Europe*, SME Technical Paper FC-260, Society of Manufacturing Engineers, Dearborn, MI (1987).
258. Simpson, J. T., *Radiat. Phys. Chem.*, 25, p. 483 (1985).
259. Pacansky, J., and Waltman, R. J., *Prog. Org. Coat.*, 18, p. 79 (1990).
260. Goldberg, E. P., et al., U.S. Patent 6,387,379 to University of Florida (2002).
261. Salovey, R., et al., U.S. Patent 6,281,264 to the Orthopedic Hospital, Los Angeles, and University of South California, Los Angeles (2001).
262. Perez, E., Miller, D., and Merrill, E. W., U.S. Patent 5,836,313 to Massachusetts Institute of Technology (1998).
263. Hasegawa, T., and Kondo, T., U.S. Patent 6,127,438 to Asahi Kasei Kogyo Kabushiki Kaisha (2000).
264. Nablo, S. V., U.S. Patent 5,825,037 to Electron Processing Systems, Inc. (1998).
265. Kaetsu, I., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Publishers, Munich, Chapter 8 (1992).
266. Wendrinsky, J., *RadTech Europe 2001*, Basel, Switzerland, October 8–10 (2001).

# 6

## *Coating Methods Used in UV/EB Technology*

There are numerous methods of applying liquid systems to different surfaces, and the following sections will discuss some of them. Many of these techniques are used in both UV and EB curing processes. Some are very specific to UV technology, and these will be dealt with separately in connection with that curing method.

## 6.1 Roll Coating

Roll coating is widely used as an efficient way to coat uniform, generally flat or cylindrical surfaces of rigid or flexible substrates. There are many types of roll coating methods; the two most common are *direct roll coating* and *reverse roll coating.*

### 6.1.1 Direct Roll Coating

In direct roll coating, the sheets or stock to be coated pass between two rollers, an *applicator roller* and an *impression* (or *backup*) *roller*, which is being rotated in opposite directions. Thus, the material being coated is pulled by the rolls. The applicator roll is usually covered with a relatively hard elastomeric compound. The coating is fed to the applicator roll by a smaller *feed* or *doctor* roll that is in turn fed by a *pickup roll*. The pickup roll runs partially immersed in a tray called *fountain*, containing the coating.[1] As the coated material comes out of the nip between the rolls, the wet layer of the coating is split between the applicator roll and the substrate. The film thickness is controlled by the clearance between the feed roll and the applicator roll. The arrangement for direct roll coating is in Figure 6.1.

Several variations of direct roll coating are possible by using different types of applicator rolls. For example, the entire surface of the applicator roll may consist of engraved small recessed cells (see Figure 6.2). The cells are filled with coating, the surface is scraped clean with a *doctor blade*, and the coating is transferred to the substrate being coated. This type of roll is referred to as a *gravure applicator roll*.[2] Besides being employed in precision coating, this type of roll finds use in printing (see Section 7.5.5). The engraved roll can be
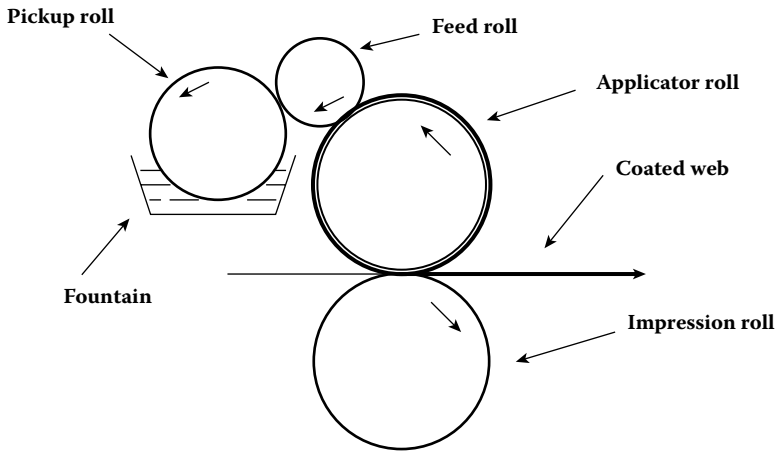
**FIGURE 6.1**
The arrangement for direct roll coating.

partly immersed in the coating pan, so that the fountain and feed rolls are not needed.

## 6.1.2 Reverse Roll Coating

In reverse roll coating the two rolls are rotating in the same direction and the material being coated has to be moved through the nip by means of a drive roll. The coating is applied by wiping rather than film splitting and is picked up by the web moving in the reverse direction. The coat weight can be exactly controlled by the gap between the metering and application rolls. Reverse roll coating is suitable for applying high-viscosity coatings onto flexible substrates, and the result is a smoother film than that obtained by direct roll coating.[1,2] The arrangement for reverse roll coating is in Figure 6.3. A variety of possible arrangements for roll coatings is shown in Figure 6.4.
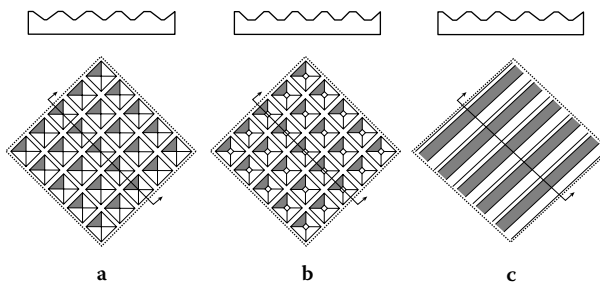


**FIGURE 6.2**
Different types of cells on the surface of a gravure roll: (a) pyramidal, (b) quadrangular, (c) trihelical. (Courtesy of Flexographic Technical Association.)
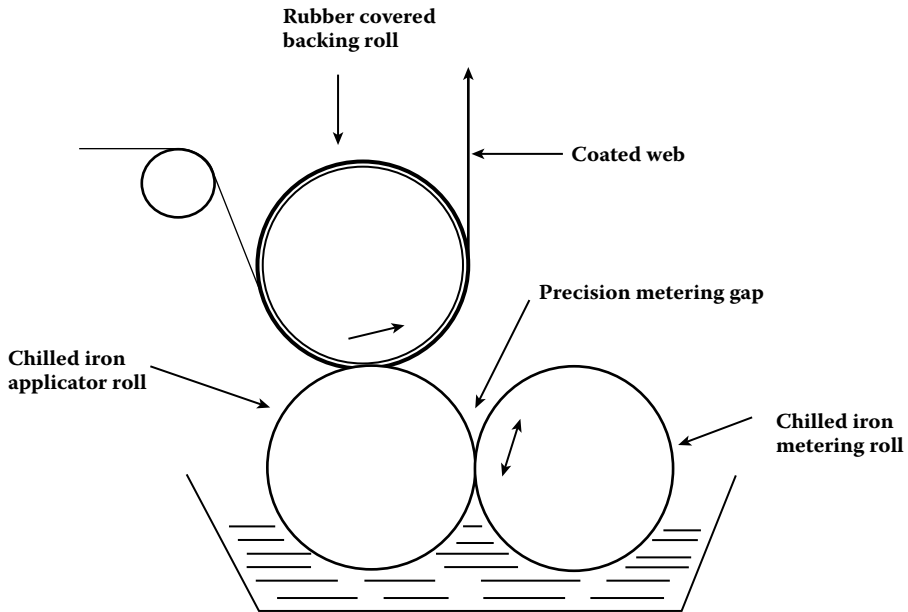
**FIGURE 6.3**
Reverse roll coating.

## 6.2 Curtain Coating

Curtain coating is widely used in the coating of flat sheets of substrate, such as wood panels. A coating is pumped through a slot in the *coating head* so that it flows as a continuous *curtain* of liquid. The material to be coated is moved under the curtain by a conveyor belt. The curtain is always wider than the substrate, and therefore a recirculating system is necessary for the overflow from the sides.

The film thickness is controlled by the width of the slot and the speed of the substrate being coated; the faster the speed, the thinner is the coated wet film. Because there is no film splitting, the coating is laid down essentially smooth.[1]

## 6.3 Spray Application

Spray application is widely used for applying coatings and paints in industrial and architectural applications. It is particularly well suited for surfaces with irregular shape, although it can be used also for flat surfaces, if other methods, such as roll or curtain coating, would not be feasible. The main disadvantage of spraying is the difficulty of controlling where the paint goes
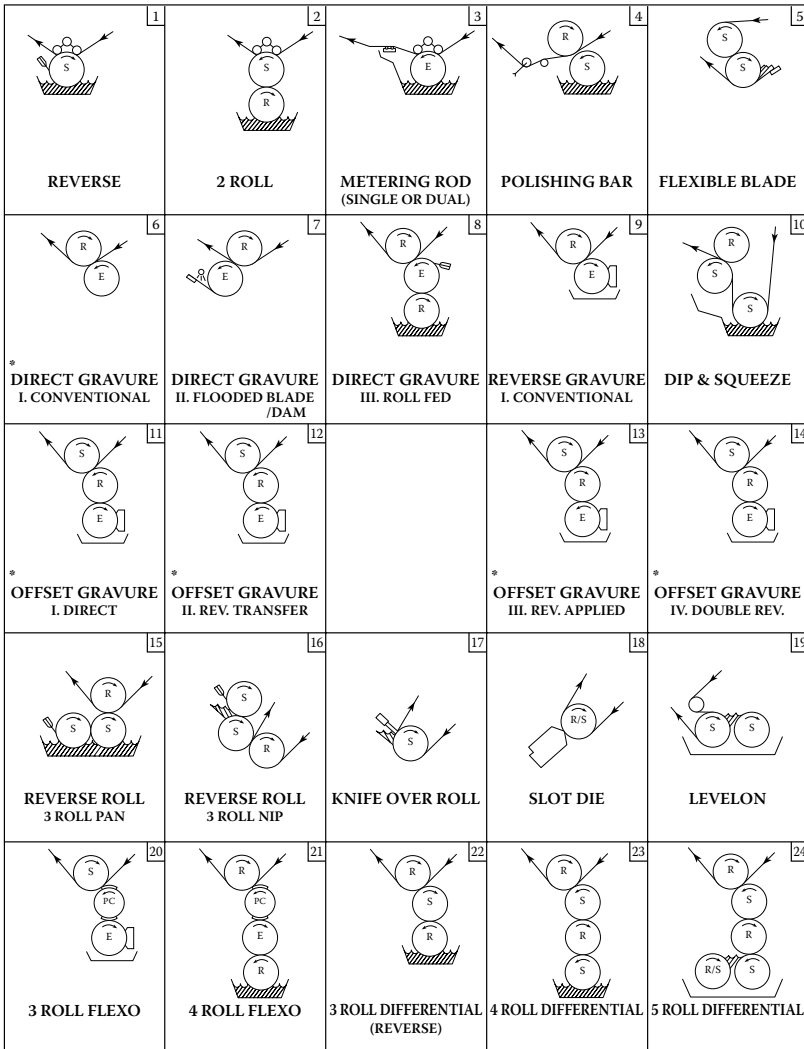
**FIGURE 6.4**
Different roll coating methods and roll arrangements: S = steel roll, R = rubber-covered roll, E = engraved roll. (Courtesy of Faustel Corporation.)

and the inefficiency of application, since only a fraction of the spray particles are actually deposited on the object being sprayed.

There are many different kinds of spraying equipment used for coatings; they all atomize the liquid into droplets. The droplet size depends on the type of spray gun and coating. The variables affecting it are air and liquid pressure, liquid flow, viscosity, and surface tension.

### 6.3.1  Compressed Air Gun Spraying

The oldest method, still in use today, is employing compressed air guns, in which the stream of liquid is driven through the nozzle orifice by pressures of 1–5 kPa (1.5–7 psi). In general, compressed air guns are less expensive than other spray guns. Atomization can be finer than with other methods. The system is versatile, and virtually any sprayable material can be sprayed with air spray. Improved transfer efficiency is achieved by *high-volume, low-pressure* (HVLP) air guns. These operate at low air pressures, typically 2–7 kPa (3–10 psi), and at a much higher air volume than standard spray guns.[1] Spray guns can be handheld or attached to robots.

### 6.3.2  Airless Gun Spraying

In airless spray guns the liquid is forced out of the orifice at high pressure, anywhere from 5 to 35 MPa (725 to 5,075 psi). As the liquid comes out of the orifice, the pressure is released, resulting in cavitation that leads to atomization. The atomization is controlled by the viscosity (higher viscosity, larger particles), pressure (higher pressure, smaller particle size), and surface tension (lower surface tension, smaller particle size). Air-assisted airless spray guns are also available; the atomization is airless, but there are external jets to help shape the fan pattern.[3] Both handheld and robot airless guns are available.

## 6.4  Dip Coating

The object to be coated is dipped into the tank full of coating and pulled out, and the excess coating drains back into the dip tank. To minimize the thickness differential the rate of withdrawal is controlled.

## 6.5  Flow Coating

Objects to be flow coated are coated on a conveyor through an enclosure in which streams of coating are squirted on them from all sides.[3] The excess material runs off and is recirculated through the system. There is still some thickness gradation, but much smaller than in dipping.

## 6.6  Spin Coating

Spin coating utilizes centrifugal forces created by a spinning substrate to spread a liquid evenly over its surface. Current applications are in photoresist technology for the microelectronic industry and in the manufacture of

protective overcoats and adhesives for the optical storage industry (compact disks and DVDs).[5]

## 6.7  Rod Coating

*Wire-wound rod* (*Meyer rod*) is suitable for coating flat flexible surfaces with low-viscosity liquids. Its function is to remove excess liquid from the moving substrate, thereby leveling the surface of the substrate. This surface shaping is often used to achieve high-gloss coating. Usually, the rod rotates in order to avoid collection of dirt particles on it. The wet thickness of the coating depends on the diameter of the wound wire, fluid rheology, web speed, and rotation of the rod.[5] Similarly, smooth bars, blades, or air knifes are used for the same purpose. If coatings applied by these methods have insufficient surface smoothness, casting against a polished chrome-plated drum or a quartz cylinder is a relatively simple method to achieve coating surface with nearly optical quality. The topology of the casting cylinder surface is reproduced by the coating brought to the contact with the cylinder. Within a certain angle of rotation the coating is irradiated by a UV source and the coated web is removed from the drum.[5]

Some coating methods and their characteristics are summarized in Table 6.1.[5,6] The numbers are only rough guidelines.

## 6.8  Vacuum Coating

In vacuum coating, the substrate is fed through an entry template into the application chamber and leaves through an exit template. A vacuum pump or pumps generate vacuum in the system. The negative pressure causes air to be pulled into the application chamber through the entry and exit templates.

**TABLE 6.1**

Coating Methods, Characteristics, and Corresponding Coating Thickness

| Coating Method | | Coating Viscosity, Pa.s | Coating Speed, m/min (ft/min) | Coating Thickness, µm |
|---|---|---|---|---|
| Roll coating | Forward | 0.2–1 | 300 (985) | 10–200 |
| | Reverse | 0.1–50 | 150 (495) | 4–400 |
| Gravure | | 0.001–5 | 700 (2,300) | 1–25 |
| Rod (incl. wire wound) | | 0.02–1 | 250 (820) | 5–50 |
| Cast coating | | 0.1–50 | 150 (490) | 5–50 |
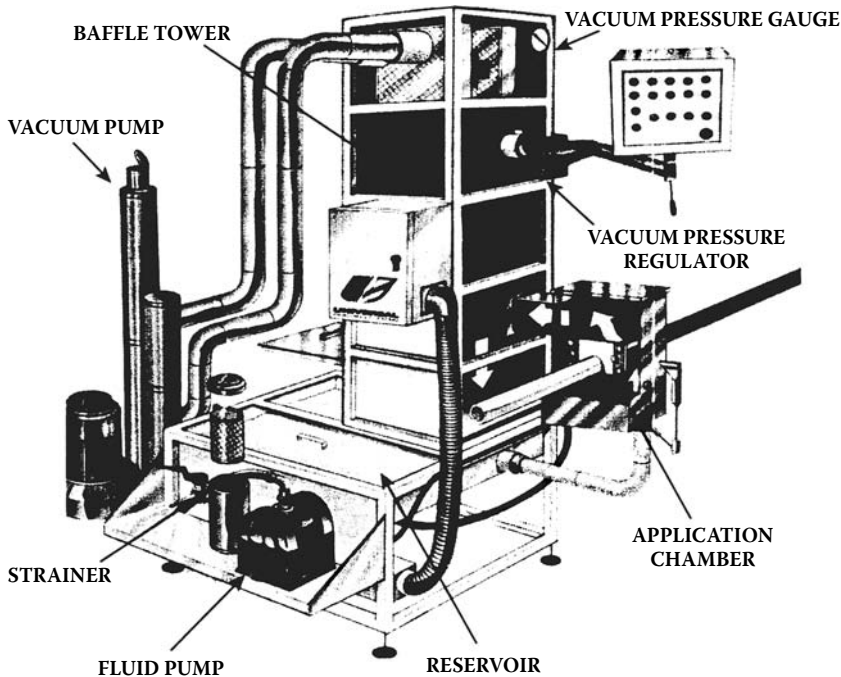
**FIGURE 6.5**
Diagram of vacuum coating system. (Whittle, K., *RadTech Report*, 18, No. 6, RadTech International N.A., p. 18 (2004). By permission from RadTech International, N.A.)

This air causes the coating material to be brought into contact with the substrate.[7] A diagram of vacuum coating system is in Figure 6.5.

The excess coating is removed and is pulled back into the baffle tower, and air and coating are separated. Air is pulled through the system toward the vacuum pump. The coating returns to the reservoir for recycling. The coating weight can be controlled by the regulation of the vacuum: the higher the vacuum inside the system, the less coating is applied to the substrate. Vacuum coating is best suited to applying coatings to moldings and round (pole-type) products. Its major advantage is that all four sides of the molding are coated in one pass.

## References

1. *Organic Coatings: Science and Technology*, Vol. II (Wicks, Z., Ed.), Wiley-Interscience, New York, Chapter XII (1994).
2. Pasquale III, J. A., *Converting*, 19, No. 12, December, Special Report, p. 62 (2001).

3. Easton, M. E., *J. Oil Colour Chem. Assoc.*, 66, p. 366 (1983).
4. Taylor, J. F., *Spin Coating: An Overview and Guide*, www.radtech.org/Applications (September 2000).
5. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. I, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 184 (1998).
6. *Modern Coating and Drying Technology* (Cohen, E. D., and Gutoff, E. B., Eds.), VCH, Weinheim (1992).
7. Whittle, K., *RadTech Report*, 18, No. 4, July/August, p. 18 (2004).

# 7

## *Applications of UV Radiation*

In previous chapters, it was shown that both ultraviolet radiation (photons) and electron beam energy (high-energy electrons) have the capability to convert certain liquid systems into solids. Although there are some areas of industrial applications, where both curing methods work, the choice of the equipment and process will depend on several factors, such as capital cost, production volume, and variety of products. Electron beam equipment usually represents a major capital investment and favors large-volume production of single or not more than a few products. On the other hand, it is capable of penetrating thicker layers, both clear and opaque, and generally works with simpler chemistry. Recent developments in both technologies, such as improved UV equipment and photoinitiators on the one hand, and low-voltage, much less expensive EB processors on the other, have further increased the number of choices. Thus, the final selection can be made only after a thorough analysis.

In this chapter, we will focus on applications where at the current state of technology UV radiation offers pronounced advantage or is the only known method for that application. Chapter 8, dealing with applications using EB, is written in the same fashion.

In contrast to currently available electron beam equipment, UV curing hardware is available in a multitude of different sizes, designs, power, in-line, off-line, in combination with large coating or printing machines, together with alternative drying equipment, as well as stand-alone units. The selection of the type of UV curing equipment is then done with regard to the process, including the substrate, the coating, paint, adhesive, or ink to be used, and the configuration of the part to be irradiated. Substrates to be irradiated can be two-dimensional, cylindrical, and three-dimensional, or the application can require only the irradiation of small areas (spot cure). The UV curing system can also be part of robotics applications.

The main technical and design issues to be resolved are:[1]

- Cure efficiency
- Heat management
- System reliability
- Suitable integration into the production line

The curing equipment will operate at the sufficient efficiency if a minimum UV dose (mJ/cm$^2$) or a minimum exposure time can be applied to obtain the desired degree of cure. This requires that the reactive binders and photoinitiator system match closely the emission spectrum of the UV source.

As discussed in Section 3.1, part of the electrical energy is converted into IR radiation that may be damaging to the substrate being processed. Air or water cooling and reflector design are the main factors involved. Heat management also means instantaneous stop of irradiation of a substrate that is not moving. In most cases, a properly designed shutter prevents overheating the standing substrate. When the shutter closes, the lamp power is automatically reduced to standby mode.

The system reliability not only means minimum downtime, but also implies a compliance with the quality of the curing process, and it is the manufacturer's responsibility to design it to meet these criteria.[2]

When integrating the UV curing system into the production line, attention must be paid to the following:[3]

- Master-slave operation of machine and UV curing unit in all states of operation (start, standby, and production)
- Status monitoring of electric power, shutter and reflector operation, temperature, and cooling conditions
- Easy maintenance and servicing
- Minimum effect of the UV unit on machine parts (no excessive heating or ozone-induced corrosion)

Uniformity of the supplied energy from the radiation source is crucial to produce a uniform finished coat. There are essentially three possible arrangements:

- A *single array*, which may be a single lamp sufficiently long to cover the width of the web being processed, or several shorter sources covering the width. Clearly, such arrangement is used for flat or slightly curved webs or very simple shapes. This setup is used widely for printing or wood finishing.
- A *multiple array* usually consists of ten to twelve lamps and adjustable carriages. It is suitable for irradiating parts with complex shapes or many different shapes of parts. The arrangement allows focusing the light on all coated surfaces.
- The *robotic array* is best suited for complex geometries. It uses the same type of robot that applied the coating, and the system has a single source of radiation for each robot. An example of using robotics for UV cure is in Figure 7.1.

UV technology is becoming more dispersed over more markets due to its acceptance in markets that did not use it a decade ago, such as metal coatings
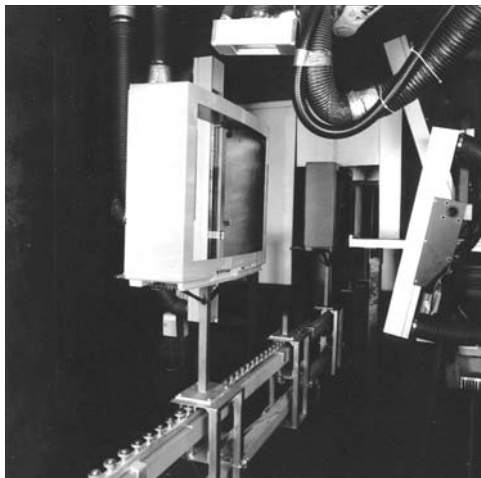
**FIGURE 7.1**
3D UV curing using robotics. (Courtesy of IST Metz.)

and exterior applications. The wood market is still expanding mainly due to environmental concerns (primarily emissions) and improving efficiency.

On the other hand, the automotive original equipment manufacturing (OEM) sector is the slowest market due to the extensive testing that has to be done on coatings. Another factor here is the recent slowdown of the economy in general and of the automotive industry in particular.

The refinishing side of the automotive market is growing considerably faster, because the applications have been developing over the past decade and represent numerous advantages, such as efficiency and improved environment, due to drastic reduction of the use of solvents and due to improved practices.

## 7.1 UV Curing of Coatings and Paints

### 7.1.1 Functional and Decorative Coatings

#### 7.1.1.1 Coatings on Flat, Rigid Substrates

UV curable coatings are applied to a variety of flat, rigid substrates, such as particle board, medium- and high-density fiberboard, wood veneers, polycarbonate, poly(methylmethacrylate), paper, and metal sheets and foils. An example of a formulation for UV curable coatings is in Table 7.1.

UV curing units are an essential part of the coating line, consisting typically of the following main components:[4,5]

1. Infeed
2. Substrate preparation

**TABLE 7.1**

Example of a UV Coating Formulation

| Ingredient | Typical Amount, Weight % | Function |
|---|:---:|:---:|
| Pepolymer (oligomer) | 25–95 | Film forming, affects film properties |
| Monomer (reactive thinner) | 0–6 | Viscosity adjustment, contributes to film forming |
| Fillers or pigments | 0–60 | Cost saving, coloring, improve sanding |
| Photoinitiator | 1–5 | Initiates UV-induced polymerization |
| Miscellaneous additives, defoamers, matting agents | 0–3 | Affect processing behavior and appearance of finished film |

3. First coating station

4. First UV curing unit

5. Second coating station

6. Second UV curing unit

7. Last coating station

8. Last UV curing unit

9. Outfeed

As a general procedure, the first step is preparation of the substrate, which may include cleaning, sizing, and applying thin overlay by lamination to cover surface imperfections. Metal surfaces often need a primer coat to ensure a good bond of the first coat to the metal. Then the first coat is applied to the pretreated substrate. Subsequently, a second coat, often a pigmented color, is applied if desired. The next coat is a sealer, followed by a top coat. An example of a UV curing process in wood coating is in Figure 7.2.

For flat surfaces, the application method depends on the coating weight. Roll coating and curtain coating are the most efficient and economical methods to apply UV coatings to flat surfaces. The maximum coating weight that can be applied by a roll is 40 g/m$^2$; the limit for curtain coatings is 80 g/m$^2$.[6]

Normally, the last UV unit should ensure an adequately thorough cure. This may be a problem for thick layers, particularly if they are pigmented. In such cases electron beam irradiation would be the preferred curing method.[6]

### 7.1.1.2  UV Curing of Coatings on Flexible Substrates

Coatings for flexible substrates are mostly reactive systems with no solvents. Since they are usually highly viscous, they tend to produce rough surface.

| Filler | Color Coat | Seal Coat | Top Coat |
|---|---|---|---|
| **Roll Coating** | **Roll Coating** | **Roll Coating** | **Roll Coating** |
| **Physical Drying, Cure** | **Partial UV Cure** | **Partial UV Cure** | **Final UV (EB) Cure** |
| **Sanding Surface Cleaning** | **Sanding Surface Cleaning** | **Sanding Surface Cleaning** | |
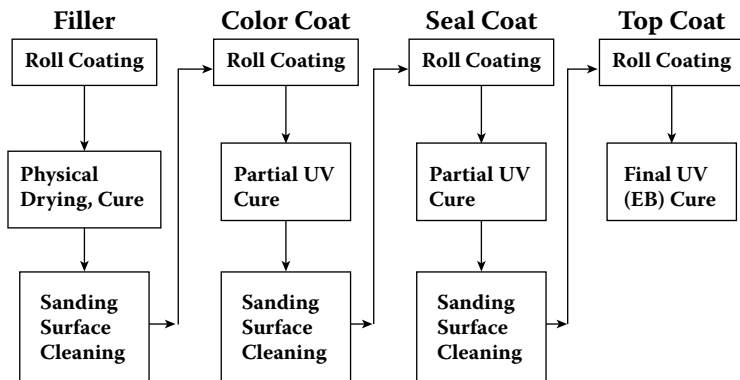
**FIGURE 7.2**

Example of UV curing of wood coatings. (Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, SITA Technology Ltd., p. 173 (1998). With permission from SITA Technology Ltd.)

Therefore, the selection of the proper application method is crucial. The selection is determined by the following factors:[7]

- Coat weight (layer thickness)
- Coat viscosity and viscoelasticity
- Coat weight accuracy required
- Coating speed
- Substrate to be coated

Roll coating is the preferred method for most coatings applied to flexible substrates. Gravure roll coating is the most precise method, yet allowing coating speeds up to 700 m/min (2,135 ft/min).[8] Other roll coating methods, such as forward and reverse coating, are selected according to the task and depend on the viscosity of the coating and coating thickness (see Chapter 6). For higher precision and lower coating weights, multiple roll (typically four or five) systems are often employed.[9] An example of a modern coating line with multiple curing lamps is shown in Figure 7.3.

## 7.1.2 UV Curing of Lacquers, Varnishes, and Paints

The coatings include clear overprint varnishes, finish coatings for PVC, wax-less flooring, finish coatings for paper and film applied as laminates in wood decoration, and transparent functional coatings with special characteristics, such as high abrasion resistance, barrier properties, conductivity, and chemical resistance. Coat weights of clear varnishes and lacquers may vary from 2 to 5 $g/m^2$ for typical overprint applications and from 10 to 100 $g/m^2$ for finish and functional coatings. Because of the relatively low coating weights, gravure and reverse roll coating methods are used in most cases.[10]

**FIGURE 7.3**
Curing section of a modern coating line with four UV lamps. (Courtesy of Prime UV Systems.)

### 7.1.3 Three-Dimensional Curing

Because of their frequently complicated shapes, three-dimensional (3D) objects require different coating techniques, such as spray, dip, and flow and spin coating. The lamps in curing units for 3D objects are stationary and the parts pass in front of them. They usually rotate two to three times as they pass through the irradiation zone. The irradiation zone must have a shield to eliminate direct and first scattered light. Because of the complexity of coated parts and high demands on quality, UV lamps are frequently mounted on robotics (shown previously in Figure 7.1).

### 7.1.4 UV Curing of Coatings and Inks on Cylindrical-Shaped Parts

This method is used for curing coatings and inks on plastic cups, tubs, tubes, or metal cans.[11] The parts are placed on mandrels, which are attached to a rotating device. This device moves them through the individual stations: feed, pretreat (most frequently corona or flame, for plastics), printing, curing, and take-off. The printing is done by dry offset (see Section 7.5.3).

Compact and high-powered UV lamps are used to allow curing of the rotating cup directly on the mandrel. Curing times are in the range of 70 to 100 ms.[12]

### 7.1.5 UV Matting of Coatings

The impression of a matte film surface is created by the diffuse reflection of light from a micro-rough surface. Such a structure is obtained by

incorporating a matting agent (e.g., synthetic amorphous silica) or by changing the surface topology through shrinkage during polymerization.

To achieve matte surface by UV curing, traditionally, the so-called *dual-cure process* is used.[13] In the first step, the coated film is irradiated by a low dose, and the matting agent (most frequently synthetic amorphous silica) in the coating can migrate to the surface of the film. The film is then cured completely in the second step. With acrylate-based coatings, the method is modified by using metal halide lamps for the first irradiation step, whereas the final surface cure is accomplished by mercury arc lamps. Another method is based on cure inhibition by oxygen. In the first step, a matted surface is created by surface cure inhibition and the surface structure is fixed by the second cure (UV or EB).

A relatively new method uses 172 or 222 nm excimer radiation in nitrogen atmosphere.[14] The irradiation causes a surface cure of the acrylate coating similar to milk skim in appearance. In the second step, the coating is fully cured by UV or EB.

Each method and application requires specific formulation with specific properties, such as solids content, density, viscosity, color, finished film thickness, scratch resistance, gloss, etc. An example of a UV curable formulation is in Table 7.1.

## 7.2 UV Curing of Adhesives

Radiation curable adhesives represent a small but growing segment of the overall radiation curing market since they are an attractive alternative to solvent-based, water-based, and hot melt adhesives. Structural adhesives, pressure-sensitive adhesives (PSAs), laminating adhesives, and transfer metallization adhesives can be radiation cured. Commercial adhesive products made on UV/EB equipment include pressure-sensitive tapes and labels, laminated foils and films, flocked materials for automotive and shoe applications, structural bonding adhesives, and abrasive bonding systems. The technological and cost advantages of these adhesives are that they are single-component materials that can be dispensed with automatic dispensing equipment, have long open time and low energy requirements, exhibit fast cure rates, have the ability to precision bond, and exhibit low heat input to temperature-sensitive substrates.[15]

### 7.2.1 Energy Curable Laminating Adhesives

Laminating adhesives generally bond clear laminate plastic films. As long as the films are clear, the adhesive can be cured by UV energy; if they are opaque, electron beam radiation is a better choice.

PSA-type laminating adhesives can be cured prior to the lamination. The adhesive film is tacky as a typical PSA and produces good bonds. Another method involves lamination first and the cure after that. In this case the bond

**TABLE 7.2**

Formulation for UV Curable Lamination Adhesive

| Component | % wt. | Remark |
|---|---|---|
| Inert resin in TPGDA[a] | 60.0 | Base resin (elastomer) |
| Dipropylene glycol diacrylate (DPGDA) | 34.0 | Difunctional reactive diluent |
| Methacrylated phosphate ester | 3.0 | Adhesion promoter |
| Aromatic ketone | 3.0 | Photoinitiator |
| Total | 100.0 | |

[a] Tripropylene glycol diacrylate, reactive thinner.

| Test | Results |
|---|---|
| Viscosity, mPa.s | 450 |
| Reactivity, mJ/cm$^2$ | 100 |
| Adhesion, T-peel, N/25 mm | |
| OPP/OPP | SF |
| Metallized OPP/PE | SF |
| PE/PE | 3.78 |
| PE/Paper | SF |

*Note:* SF = Substrate failure.

*Specimen preparation:* Film thickness 0.3 mil (7.7 µm); the substrate was corona treated to 42 dynes/cm; adhesive cured through the laminate film using a 300 wpi (120 W/cm) mercury lamp.

strength depends mainly on the adhesion of the adhesive to the substrate; the cured adhesive film is strong, and consequently, the cohesion of the laminate is high. In many cases the bond is so strong that one or both substrates fail.[16]

Examples of laminating adhesives based on urethane acrylates are in Tables 7.2 and 7.3. The respective resulting bond strength values from varied substrates are shown. Specimens were prepared in the following fashion: film thickness, 0.3 mil (7.7 µm); the substrate was corona treated to 42 dynes/cm; adhesive cured through the laminate film using a 300 wpi (120 W/cm) mercury lamp.

## 7.2.2 Energy Curable Pressure-Sensitive Adhesives

UV curable pressure-sensitive adhesives (PSAs) are based on two types of UV curable materials:

1. Materials that already are pressure-sensitive adhesives, but can be modified by radiation (UV or EB) to introduce or increase cross-linking, which increases their adhesive properties, shear value, peel strength, service temperature range, and solvent resistance

2. Materials, such as acrylates with tackifiers, acrylate polyesters, and polyurethanes, that do not have properties as pressure-sensitive adhesives, but after cross-linking have desired pressure-sensitive properties

**TABLE 7.3**

Formulation for PSA-Type UV Curable Laminating Adhesive

| Component | % wt. | Remark |
|---|---|---|
| Monofunctional urethane acrylate in EHA[a] | 26.1 | Base resin (elastomer) |
| Modified saturated polyester resin in EHA[a] | 35.1 | Tackifier |
| 2-(2-Ethoxyethoxy)ethyl acetate | 23.6 | Inert diluent |
| Isobornylacrylate monomer (IBOA) | 5.6 | Diluent monomer |
| Aliphatic urethane acrylate | 5.6 | Reactive diluent |
| Aromatic ketone | 4.0 | Photoinitiator |
| Total | 100.0 | |

[a] 2-Ethylhexyl acrylate monomer.

| Test | Results |
|---|---|
| Viscosity, mPa.s | 560 |
| Reactivity, mJ/cm$^2$ | 500 |
| Adhesion, T-peel, N/2.5 mm | |
|   OPP/PE | 19.34 |
|   PE/PE | 10.45 |
|   PET/PE | 7.78 |
|   Metallized OPP/PE | 6.67 |
|   PE/Paper | SF |

*Note:* SF = Substrate failure.

In the past, electron beam radiation was applied to produce PSA exclusively; however, recent improvements in UV curing technology (precise UV dose control, suitable photoinitiators) permit UV to be used to produce pressure-sensitive adhesives. PSA formulations can vary in consistency from low-viscosity liquids up to solids melting at 80°C (176°F). Therefore, applications may vary from screen printing to roll coating to melt extrusion. Coat weights for most PSA materials vary from 1 to 10 g/m$^2$.

As pointed out above, radiation or energy curable adhesives can be essentially hot melts or liquids at the room temperature. For this technology, a liquid curable PSA formulation is comprised of four essential components:

1. Base resin (elastomer)
2. Tackifier
3. Diluent
4. Photoinitiator

An example of the *elastomeric component* is a combination of multifunctional and difunctional aliphatic urethane oligomers. Suitable oligomers have relatively high molecular weights and glass transition temperatures ($T_g$), which enables the adhesive to have elastic properties at room temperature. Its deformability under

light pressure allows it to conform to and wet out a substrate. Upon removal of the adhesive from the substrate, its elasticity allows it to extend greatly before separating, giving it a good tack and peeling properties.

The *tackifier* is most frequently a saturated polyester resin. It generally has a much lower molecular weight and higher $T_g$. The higher $T_g$ of the tackifying resin brings the overall adhesive $T_g$ to a value necessary to achieve pressure-sensitive properties. Typically, the $T_g$ values of PSAs range from –25 to +5°C. In general, the higher the overall $T_g$ of an adhesive, the greater the cohesive strength and high-temperature shear results, and the lower the tack and deformability properties.

The reactive monomer, besides being a *diluent*, plays a role similar to that of tackifying resin, namely, affecting the deformability of the adhesive.

The *photoinitiator* (single or in a combination) is vital to the manner in which an adhesive cures. The desired property of the PSA is a balance of good tack and good adhesion. If the state of cure is too high, the tack will be too low, and if the state of cure is too low, the adhesive will stick to the substrate, but will be difficult or impossible to remove.

The methods to evaluate PSAs include the *rolling ball test* (ASTM D3121, PSTC-6, BS EN 1721), *loop tack test* (ASTM D6195, FINAT Test Method 9, BS EN 1719), and *quick stick test* (PSTC-5).[16]

Pressure-sensitive adhesives are used in a great variety of applications, most commonly for adhesive tapes. In that case, they have to be tested by *static shear test* or *dynamic shear test*.[16] The difference between these two methods is that in static shear test a standard force is being applied to the test specimen and the adhesive failure is reported as the time it takes for failure to occur. The dynamic shear test involves a force being applied to the PSA tape at a specific rate of speed (typically 0.25 mm or 0.1 in. per minute). The value reported is as the peak force per unit area (lb/in$^2$, also abbreviated as psi, and in SI units MPa) required to cause adhesive failure. The standards for adhesion shear tests are ASTM D3654, ISO EN 1943, and PSTC-107.[17,18]

Another type of shear test involves testing under heated conditions. The shear adhesion failure test (SAFT) (FINAT FTM 8, PSTC-7) is a static shear test administered to a PSA sample under increasing temperature at a rate typically of 1 or 2°C per minute. The recorded SAFT value is the temperature at which the adhesive bond fails.

In the adhesion peel test (ASTM D3330, ISO EN 1939, PSTC-101) the force required to remove the respective adhesive from a specific substrate. Three components are involved in this process: the extension of the adhesive itself, the deformation of the PSA backing substrate during the removal process from the substrate surface and the force to remove the adhesive from the substrate. The adhesive tapes are generally removed under a 90° (T-peel test, ASTM D1976) or 180° angle at a specific rate. The result is shown as the average peeling force per unit width, i.e., lb/in. (sometimes shown as pli, and in SI units kN/m).

An example of the *high-tack UV curable* PSA formulation is in Table 7.4. The low $T_g$ and cross-linking combination of this PSA offers very high tack

**TABLE 7.4**

High-Tack UV Curable PSA Formulation

| Component | % wt. | Remark |
|---|---|---|
| Monofunctional urethane acrylate in EHA[a] | 17.0 | Base resin (elastomer) |
| Inert resin in aliphatic urethane acrylate monomer | 55.0 | Tackifier |
| 2-(2-Ethoxyethoxy)ethyl acetate | 22.0 | Diluent |
| Aromatic ketone | 6.0 | Photoinitiator |
| Total | 100.0 | |

[a] 2-Ethylhexyl acrylate monomer.

| Test | Results |
|---|---|
| Viscosity, mPa.s | 1,500 |
| Loop tack, lb/in$^2$ (MPa) | 3.49 (2.4 × 10$^{-2}$) |
| Peel strength, pli (kN/m) | 2.54 (0.43) |
| Static shear strength at RT, h | 1.25 |
| Static shear strength at 80°C, h | 0.00 |

performance, but limited cohesion, which is evident in the low shear value and negligible heat resistance. A typical *well-balanced UV curable* PSA formulation is shown in Table 7.5. This formulation offers a well-balanced PSA performance with exceptional adhesion and shear properties. This is accomplished by the use of inert tackifying resin to allow the oligomeric component

**TABLE 7.5**

Well-Balanced UV Curable PSA Formulation

| Component | % wt. | Remark |
|---|---|---|
| Monofunctional urethane acrylate in EHA[a] | 40.0 | Base resin (elastomer) |
| Difunctional aliphatic urethane acrylate in dilutant | 10.0 | Base resin (elastomer) |
| Inert resin | 25.0 | Tackifier |
| Difunctional oligoamine resin | 3.0 | Reactive resin |
| Isodecyl acrylate | 18.0 | Increases cross-linking |
| Aromatic ketone | 4.0 | Photoinitiator |
| Total | 100.0 | |

[a] 2-Ethylhexyl acrylate monomer.

| Test | Results |
|---|---|
| Viscosity, mPa.s | 5,900 |
| Loop tack, lb/in$^2$ (MPa) | 1.70 (1.2 × 10$^{-2}$) |
| Peel strength, pli (kN/m) | 6.40 (1.1) |
| Static shear strength at RT, h | Indefinite |
| Static shear strength at 80°C | Indefinite |

to maximize its elastic characteristics and to decrease the cross-link density, which increases the tack and peel properties while still maintaining very good shear and heat resistance.[19]

### 7.2.3 Energy Curable Assembly Adhesives

UV curable adhesives have been used in electronics and electrical manufacturing operations for many years. There are many uses, such as bonding of coils, bonding of loudspeaker membranes, bonding and sealing of wires in ducts, bonding of liquid crystal displays, and bonding of membrane switches.[20]

Another well-established use of UV/visible light curing adhesives is glass, a plastics bonding in the automotive industry. Typical applications are lamination of safety glass, fastening of rear-view mirrors to windshields, and assembly of headlights.[20]

In the medical field, UV curable adhesives are used in the assembly of medical devices, such as syringes, valves, manifolds for filtering equipment, and arteriographs. In these applications, many dissimilar substrates, such as stainless steel, aluminum, glass, polycarbonate, polymethyl methacrylate (PMMA), PVC, and other thermoplastics, are bonded.[21]

Light curing cyanoacrylate adhesives are suitable for high-speed assembly processes. These one-part, solvent-free systems offer rapid cure of exposed and confined adhesive on bond joints without requiring the use of heat or racking of parts. The bonds exhibit good environmental and thermal resistance, high strength, and a wide range of physical properties. Since they also cure by absorption of moisture, this dual-curing system reduces cure problems in shadow areas. They cure via an anionic mechanism that is not inhibited by oxygen. With special primers, cyanoacrylates form good adhesive bonds with polyolefins and fluoropolymers. The limitations of light curing cyanoacrylates are blooming/frosting, they may cause stress cracking of some plastics, and they are limited to cure through a gap of about 10 mils (0.25 mm).[22]

## 7.3  UV Cured Silicone Release Coatings

Silicone release liners are used as a nonadhering surface to which adhesive materials, such as, for example, pressure-sensitive adhesives, can be laminated. UV curable release coatings are based on poly(dimethylsiloxane) oligomers functionalized with acrylate or epoxy groups and are mostly coated onto papers or thin films.

The coat weights are critical for the release properties of the liner. They are typically in the 0.7 to 1.0 g/m² range and are applied most frequently by multiroll reverse coating systems or by offset gravure rolls.

The chemistry involved depends on the oligomer used: silicone acrylates cure by radical mechanism; epoxy-silicones require cationic curing systems. Silicone

acrylates are exceptionally sensitive to oxygen and require nitrogen inertization in the curing zone. Epoxy silicones are not oxygen sensitive, and therefore the cure can be done in air. However, for high-speed applications the humidity in the reaction zone should be kept low to ensure stable curing conditions.[23]

Since temperature-sensitive substrates, such as paper and thin thermoplastic films, and high line speeds (up to 600 m/min or 1,970 ft/min) are used, irradiator heat management and power management are of great significance. The curing systems can consist of medium-pressure mercury lamps or electrodeless medium-pressure lamps. If needed, the irradiators are placed above a cooled drum carrying the substrate. Dielectric barrier-discharge-driven excimer lamps can be also employed as a completely cold source of radiation for exceptionally sensitive substrates.[24]

## 7.4 Spot Curing

Spot curing is used in curing adhesives and dental compositions. Dental curing systems use 35–75 W tungsten filament quartz halogen tubes. The wavelength range used in such a system is 400 to 500 nm, with a typical irradiance of 500 mW/cm². Adhesives are typically cured with a short 100 W arc mercury lamp coupled to a UV transmitting waveguide.[24] There are other lamp systems used for different applications. An example of a spot curing lamp is in Figure 7.4, and a small-area vertical curing system operating



**FIGURE 7.4**
Spot curing lamp. (Courtesy of Dymax Light Curing Systems.)

**FIGURE 7.5**
Mercury-xenon lamp for small area curing. (Courtesy of Hologenix Company.)

with a 200 W mercury-xenon lamp at 365 nm is in Figure 7.5. These sys-
tems are used in the electronic industry (e.g., for assembly of printer heads)
and in medical applications (e.g., attaching dispensing needle to the syringe
barrel).[25] A flood curing lamp used for somewhat larger areas is in Figure 7.6.
LED curing equipment is shown in Figures 7.7 and 7.8.

**FIGURE 7.6**
Flood curing lamp. (Courtesy of Dymax Light Curing Systems.)



**FIGURE 7.7**
LED curing lamp. (Courtesy of American Ultraviolet Company.)

**FIGURE 7.8**
Floor cure LED equipment. (Courtesy of American Ultraviolet Company.)

## 7.5  UV Curing in Printing and Graphic Arts

The objective of printing is to create a visibly identifiable image, consistently, for a large number of impressions. In principle, this can be done with a printing plate, and the various printing methods are named after the nature of the printing plate. Many techniques have been developed for this purpose.

**TABLE 7.6**

Printing Ink Viscosity Ranges

| Printing Method | Viscosity @ 25°C, mPa.s |
| --- | --- |
| Gravure | 30–200 |
| Flexography | 50–500 |
| Newsprint ink | 200–1,000 |
| Screen printing | 1,000–50,000 |
| Letterpress | 1,000–50,000 |
| Lithography | 10,000–50,000 |

Flexography, lithography, and gravure are the main printing techniques, which account for the vast majority of printing applications. Each of these methods has a number of variations. For example, the viscosity of printing inks has to be matched to the printing method. Typical values of viscosities of printing inks are in Table 7.6.

Graphic arts are a well-established application of UV curing worldwide. Essentially, the processes used in graphic arts include the generation of images to be reproduced onto the printing plate, silkscreen, etc., and the use of radiation curable inks and overprint varnishes. Many imaging processes rely on the exposure of materials to radiation to bring about the change in solubility in a solvent system (organic or aqueous), thus enabling exposed and unexposed areas to be differentiated. The differentiation between exposed and unexposed areas can lead to selective delamination, softening, tackiness (which may affect the adherence of toner powders), or a change in refractive index, which leads to holographic effects.

### 7.5.1 Screen Printing

The screen printing process uses a rubber squeegee to force ink through a tightly stretched, finely woven mesh onto various substrates. The basic concept has been refined to the point where large semi- and fully automatic lines are relatively common. Typical products are display printing, industrial and container printing, and printed circuit production.[25]

Traditionally, evaporation-drying solvent-based inks have been used. These have been replaced during the last decade by UV curable inks, which exhibit the following advantages:[26]

- UV curable inks can be applied through a much tighter mesh, which produces a lower film weight, improves resolution of fine detail, and lowers ink costs.
- More versatile than the traditional inks, and fewer grades of inks are needed for sufficient adhesion to a variety of substrates.

- Almost instantaneous cure, reduces seeping into substrate.
- High web speed under UV lamp greatly reduces distortion of substrate.
- No drying on screens; thus, screen cleaning is all but eliminated.
- Absence of solvents can eliminate the need for costly solvent recovery systems.
- UV dryers for display printers take up only a fraction of the space occupied by traditional hot-air-jet dryers.
- More abrasion and solvent resistant than the traditional inks.
- Friendly to environment, practically no health hazards.

Disadvantages cited are cost of raw materials and cost of installation of the UV curing equipment.[26]

Screen printing of UV inks is being done over paper, metal, films, foils, plastics, and PVC. Radiation curable materials are being used as vehicles for ceramic inks that are screened onto automotive windshields, cured, and then fired in an oven to burn off the organic binder and fuse the ceramic into the glass windshield.[27]

### 7.5.2 Flexography

Flexography is a mechanical printing process that uses liquid ink and a fairly soft relief image printing plate made of rubber, or more commonly photopolymer and pressure, to create an image. Completed printing plates are mounted with adhesive onto a metal cylinder that rotates against the substrate during printing. A typical flexographic printing station is shown in Figure 7.9. A chambered doctor blade ink fountain applies ink to the engraved *transfer*, or *anilox*, *roll.* The engravings on the anilox roll meter the correct amount of ink, depending on the engraving geometry and depth. The ink is transferred to the raised surfaces of the printing plate attached to the plate cylinder. The substrate is passed between the plate cylinder and the impression cylinder to achieve ink transfer.

The process is used mainly for package printing. All flexographically printed packaging substrates are web fed with the exception of corrugated board. Unlike other major mechanical printing processes (namely, lithography, gravure, and letterpress), flexography is in a phase of rapid development and change. Flexography is currently the major package printing process, and it is very unlikely that this position will change over the next few years, even in the light of digital printing technology.

The greatest strengths of UV flexography are its versatility and cost-effectiveness. Since UV inks do not dry until they pass under the UV lamp, the ink stays completely open. Unsightly print defects like dot bridging
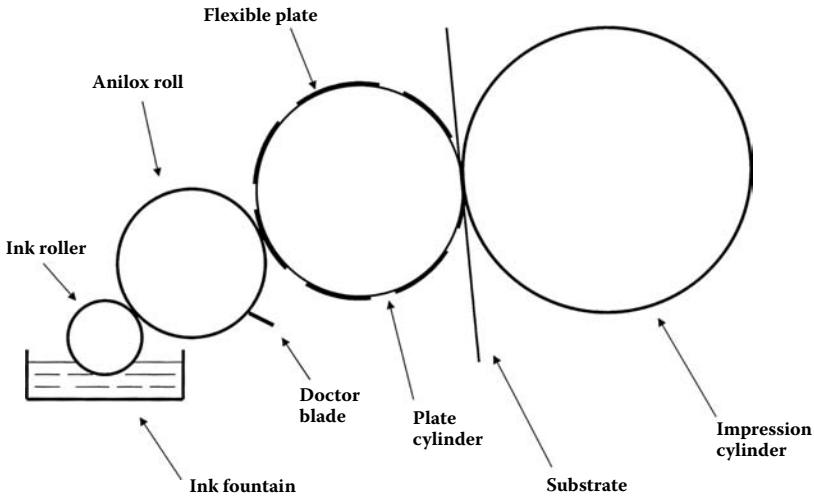
**FIGURE 7.9**
Flexographic printing deck. (Courtesy of Foundation of Flexographic Technical Association.)

caused by dried ink on the printing plate are all but eliminated. In summary, the main advantages of UV flexography over traditional technology are:[28]

- Improved repeatability for printed spot colors
- High-definition process printing: better dot structure, lower dot gains
- Efficient job setup time

The major use for UV flexo printing is a wide range of packaging products, including:

- Corrugated cases
- Folding cartons
- Liquid packaging containers
- Flexible packaging
- Multiwall sacks
- Paper bags
- Labels
- Paper cups
- Containers and closures

UV inks have been readily and successfully adopted by flexographic label printers; many of them had several years of experience with letterpress UV
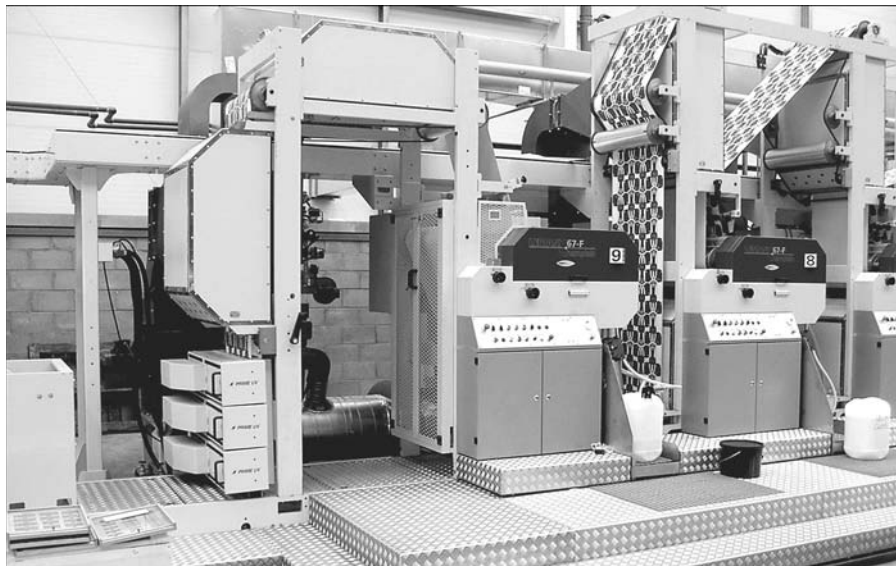
**FIGURE 7.10**
Modern flexographic folding carton press with three UV processors. (Courtesy of Prime UV-IR.)

systems. Since in flexography the common thickness of the printed ink is typically 2 to 4 µm, it is often necessary to cure individual layers of inks by UV in multicolor printing. With radical UV curable flexographic printing inks it is possible to achieve printing speeds of 250 m/min (750 ft/min) or even more.[29] A modern flexographic folding carton press with three UV processors is in Figure 7.10.

### 7.5.3 Letterpress and Offset Letterpress (Dry Offset)

The letterpress uses hard plastic or sometimes metal plates[30] and works with heavy pastes that have to be metered by a complicated series of rollers. Cylindrical objects such as two-piece metal cans have no point against which to register printing stations. This can be resolved by using a process known as *offset letterpress* or *dry offset*. In dry offset, the inked images from the letterpress printing plates are transferred onto an intermediate resilient rubber blanket roll, where all colors can be assembled in complete register. The blanket roll is then rolled against the round object, and all the colors that make up the image are transferred at one time and in complete register. Offset letterpress is shown schematically in Figure 7.11.

Dry offset is used to decorate drawn and ironed metal cans, round plastic tubs, and plastic or metal collapsible tubes.[30]
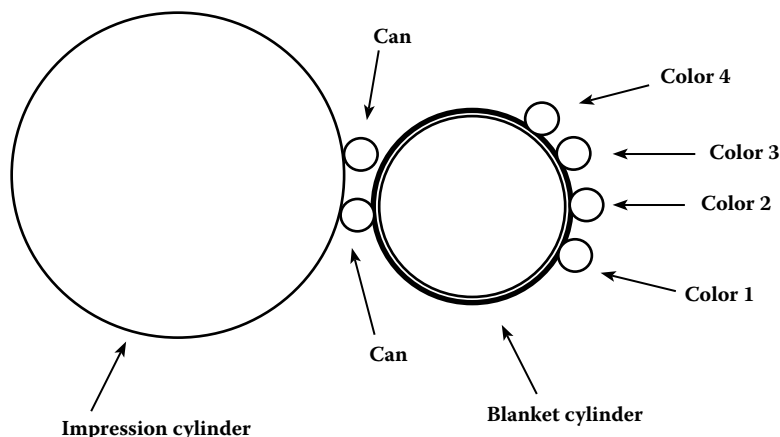
**FIGURE 7.11**
Offset letterpress (dry offset).

## 7.5.4 Lithography

Lithography is a planographic process, meaning that the printing and nonprinting areas are on the same plane. Modern offset lithography uses oil-based inks in the form of heavy paste that is metered to the plate cylinder by a train of inking rollers. Another group of rollers applies a thin film of water to the water-receptive areas. Aluminum alloy printing plates are mounted onto a plate cylinder similar to that used in lithography. The ink image transfers from the plate to the blanket roll. An impression cylinder provides the backing needed to develop slight pressure needed for transferring ink from the blanket to the substrate. UV lithographic printing is the oldest and largest of the energy curable printing technologies. It is divided into sheet-fed and web printing.[31]

Offset lithography is the most common paper printing process, used for folding carton stock and for can and bottle labels. Most lithographic presses are sheet fed, although there are some web-fed presses. A particular application of offset lithography is the printing of flat metal sheets, which are then formed into metal containers.[30] A schematic of a lithographic printing station is in Figure 7.12.

Sheet-fed lithographic printing with UV curable inks is the largest UV ink printing process, followed by UV web lithography, UV screen printing, UV flexography, UV letterpress, and UV inkjet. UV lithographic printing on sheet-fed presses is used mainly for various types of retail folding cartons, commercial printing, metal cans, labels, and food packaging folding cartons.[31]
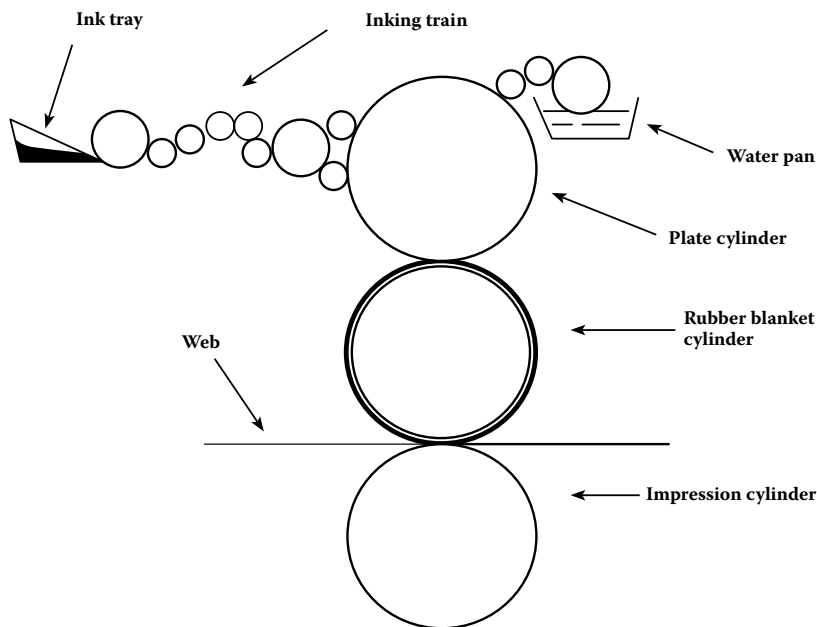
**FIGURE 7.12**
Lithographic printing station. (Courtesy of Foundation of Flexographic Technical Association.)

## 7.5.5 Rotogravure Printing

Gravure printing separates printing from nonprinting areas by an engraved pattern that is chemically etched or mechanically cut into a surface of a hollow metal cylinder. Gravure cylinders are made from copper-plated steel. The printing pattern can be photographically imposed onto the cylinder surface and chemically etched, or it can be imposed by a laser engraved with a stylus.

Normal gravure printing is done from rolls and in web form. The entire surface of the gravure cylinder is flooded with low-viscosity ink and then wiped clean with a straight-edged doctor blade. The ink remains inside the recessed cell pattern. The substrate to be printed is nipped between the impression roll and the gravure cylinder, and the ink is deposited on the substrate. Gravure printing is used for large-volume applications, such as labels, cartons, carton wraps, and flexible packaging materials.[29] A rotogravure printing station is shown schematically in Figure 7.13, and an example of a pattern on the gravure cylinder in Figure 6.2 (see Section 6.1.1).

Besides printing and decoration, flexographic, gravure, and lithographic plates as well as silk screens are used in resist chemistry, which is widely employed in the production of printed circuit boards. A resist is a material that will resist solvent attack. A negative resist is a material that, upon exposure to light cross-links, becomes less soluble in a solvent system that would
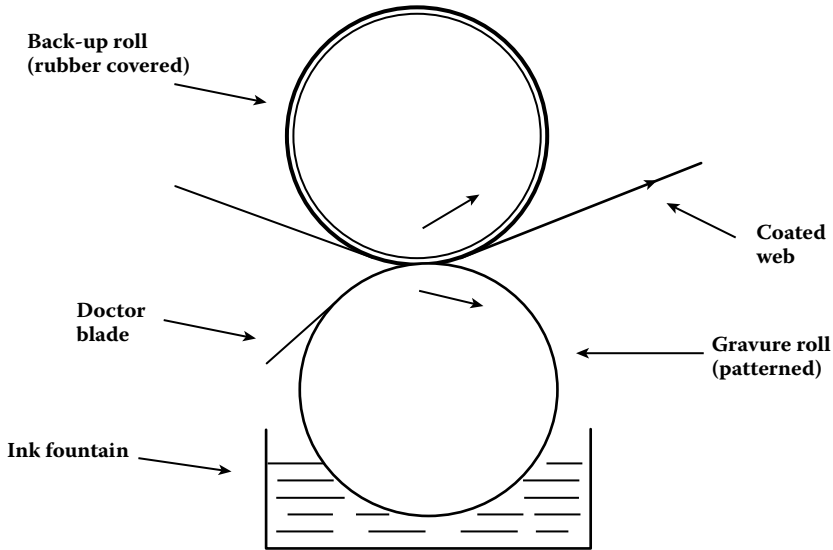
**FIGURE 7.13**
Rotogravure printing station.

dissolve nonirradiated material. A positive resist is a material that becomes more soluble after irradiation due to depolymerization.[32]

A typical printing line with UV curing lines is in Figure 7.14.

## 7.6 Rapid Prototyping

Rapid prototyping or stereolithography or three-dimensional object curing is a photochemical process used to produce solid three-dimensional objects, such as models, masters, or patterns with any shape directly from a design,
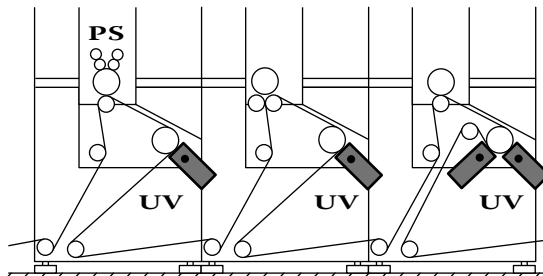


**FIGURE 7.14**
Printing line with UV curing lamps. PS, printing station; UV, UV curing lamps. (Courtesy of IST Metz.)

generated on a computer. The computer is used to control the illumination system that builds up the object, usually by a polymerization process. An important part of the design is that the object is sectioned into many small slices so that the polymerization process can be used to build up the object by adding slice upon slice. In the most frequently used process, a continuous wave laser is used to trace out and polymerize a resin in the shape of a slice and to fill in within this area as appropriate. When this process is completed, the next slice is assembled on top of the previously produced slice.[33,34] The objects are thus built up in thin layers 0.0005 to 0.020 in. (0.013 to 0.51 mm) thick. The object created by this process is then usually subjected to flood irradiation using a medium mercury lamp to complete the polymerization process.

The essential components of this process are:[34]

- A computer with a computer-aided design (CAD) or magnetic resonance imaging (MRI) software package
- A laser to provide light energy
- A mirror system for directing or focusing light energy
- A movable platform located in a reservoir (bath)
- A reservoir containing a photoreactive formulation

The software sends location information to the laser/mirror system, which then directs light energy to specific regions of a thin layer of photoreactive chemical (UV curable formulation) present on a movable platform in the reservoir. Simultaneously, the information package directs the system to lower the platform slowly with the cured slice of the object into the reservoir.[35]

The resin systems used in this process are mainly based on methacrylates and acrylates[36] and epoxies.[37] The selection of the resin system depends on the required physical properties.

## 7.7 UV Powder Coatings

The fundamental benefit of UV powder coatings is that they can be processed at considerably lower temperatures than traditional thermoset powders. While ordinary thermoset powders require temperatures in the range of 350 to 400°F (177 to 204°C), commercial UV curable powders require temperatures that are not higher than 220 to 250°F (104 to 121°C).[38] A comparison of the two types is in Table 7.7.

In contrast to the conventional powder coating, the melt and cure processes of UV curable powders are decoupled, so that while heat is used to flow the material, it does not cure the powder, and the cross-linking occurs only after the exposure to UV light. Because the temperature required for melting the

**TABLE 7.7**

Comparison of Heating and Curing Methods for Thermosetting and
UV Curable Powders

*Thermosetting Powders*

| Heating/Curing | Temperature, °C (°F) | Total Curing Time, min | Substrate |
|---|---|---|---|
| Convection | 140–220 (285–430) | 30–15 | Metal |
| Infrared + convection | 140–220 (285–430) | 25–10 | Metal |
| Infrared | 160–250 (320–480) | 15–1 | Metal |
| Induction | 240–300 (465–570) | <1 | Metal |

*UV Curable Powders*

| Heating | Curing | | | |
|---|---|---|---|---|
| IR/convection (1–2 min) | UV (s) | 90–120 (195–250) | 3–1 | Metal, wood, plastics, other |

UV curable powders is in the 175 to 250°F (80 to 121°C) range,[39] much less
heat is required, and it is needed only long enough to melt the powder, not to
cure it. Cross-linking by the UV light is nearly instantaneous; thus, the pro-
cess is finished in a fraction of the time required for conventional powders.

## 7.7.1 The Chemistry of UV Curable Powders

To be suitable for radiation curable powder coatings, materials have to contain
unsaturated double bonds. They may contain acrylic or methacrylic unsatu-
rations, but nonacrylate systems can also be used.[40] The latter is based on the
same chemistry as a commercial nonacrylate 100% reactive liquid system.
The binder consists of two components: a resin and a coreactant. The resin
is an unsaturated polyester polymer in which maleic acid or fumaric acid
is incorporated, and the coreactant is polyurethane containing vinyl ether
unsaturation. The UV curing of the binder is based on the 1:1 copolymeriza-
tion of electron-rich vinyl ether groups with electron-poor maleate or fumar-
ate groups.[41] The system contains a stoichiometric balance of maleate (ME)
and vinyl ether (VE) groups. MA/VE binder systems offer the advantage
that under controlled conditions, the components do not homopolymerize,
and that the UV curable powder coating is thermally stable. This means that
the time allotted for flow can be increased as needed. This is in contrast to
systems containing acrylic and methacrylic unsaturations because they can
react under the influence of heat alone.[40] The thermal stability of the MA/
VE systems ensures good flow and smooth films.[41] However, since they are
applied to substrates with distortion temperatures often under 212°F (100°C),
the melt viscosity has to be adjusted accordingly.[42] Another system is based

on the photoinduced cationic polymerization of solid, bisphenol A–based epoxy resins in the presence of nucleophiles as chain transfer agents.[43]

## 7.7.2 Material and Substrate Preparation

Since the binder systems are solid at room temperature, they can be produced by the existing methods used for powder coatings.[40] Solid resins, pigments, photoinitiators, and other additives are premixed, then melted and dispersed in an extruder at 100 to 130°C (212 to 266°F). The molten blend is then squeezed into a thin ribbon between chilled rolls. This ribbon is further cooled to near room temperature on a water-cooled cooling belt. The cooled ribbon is broken first into flake and then ground into a fine powder ready for use. The process is illustrated in Figure 7.15.

During the fine grinding process, the final process temperature may reach 30 to 35°C (86 to 95°F). The powder must remain free flowing at these temperatures and not soften or clump together. It is recommended to store the powder coating below 22°C (72°F), but it often happens that the containers with the powder coatings may reach 40°C (104°F) during storage and shipping.

To meet these storage recommendations, a powder must not soften below 80°C (176°F), yet must flow and level to a smooth film at 110°C (230°F). Resins, which generally have sufficiently low melt viscosity below this temperature, have a low $T_g$ and consequently low softening points. Powders from such resins could not be stored at 30°C (86°F) and probably not even at 22°C (72°F)
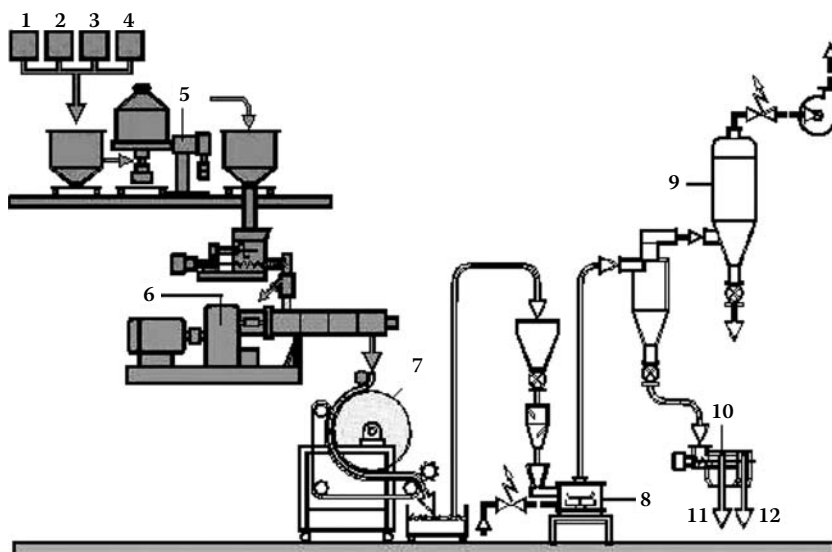


**FIGURE 7.15**
Process for preparation of powder coatings. (Courtesy of Coperion Compounding Systems.)

without problems. Thus, the melting range for UV coating powders, 110 to 120°C (86 to 248°F), is dictated only by the manufacturing and storage conditions.[44] Relative humidity during storage should not exceed 75%.[45]

Almost any substrate that will be powder coated, whether it is metal, medium-density fiberboard (MDF), or some other material, requires some kind of surface treatment. Surface preparation (pretreatment) of wood and more specifically, MDF preparation consist of sanding, removal of contaminants, and board conditioning. MDF boards that will be coated by UV curable powders should have a moisture content of 49%. It is also a common practice to preheat MDF boards prior to application of the UV powder.[45]

Metal surfaces are always cleaned by washing and usually treated by a phosphate primer. Conductive plastics are washed and dried and then coated without any further treatment. Nonconductive plastics are made conductive by applying a primer coat or treated by plasma or flame.[46]

### 7.7.3 Powder Coating Application

The coating is applied electrostatically. The powder is pumped by air through a gun, which generates an electric field and imparts a static charge to the powder particles. These charged particles are attracted uniformly to a grounded part. The part has to be conductive or coated by a conductive primer coat so that it can be grounded (see Section 7.7.2).

The powder is supplied to the gun by a powder pump at a uniform and consistent rate. There are two types of powder pumps: ejector type, using the venturi principle, and auger pumps, which use positive displacement. A corona charging system is most widely used to electrostatically charge the powder. The electrostatic spray gun has several functions:[47]

- To shape and direct the flow of powder
- To control the pattern size, shape, and density of powder
- To impart the electrostatic charge to the powder
- To control the deposition of powder on the part

Powder application is shown schematically in Figure 7.16.

The coated part is then exposed to infrared (IR) heat. The powder coat melts and forms a smooth and uniform film, which usually can take as little as only a few seconds to minutes, depending on the heat surface and the nature of the substrate. The molten film is then held at temperature until maximum flow and leveling is achieved, and then immediately exposed to a UV lamp while still molten. Cure usually takes less than 2 s.[45]

The heating phase for melting the powder is crucial to the final surface quality. The heat-up should be fast but uniform. The ovens used to melt the powder on the part can be convection, infrared, or combination (hybrid) ovens. Infrared (IR) or combination (IR/convection) ovens are most widely
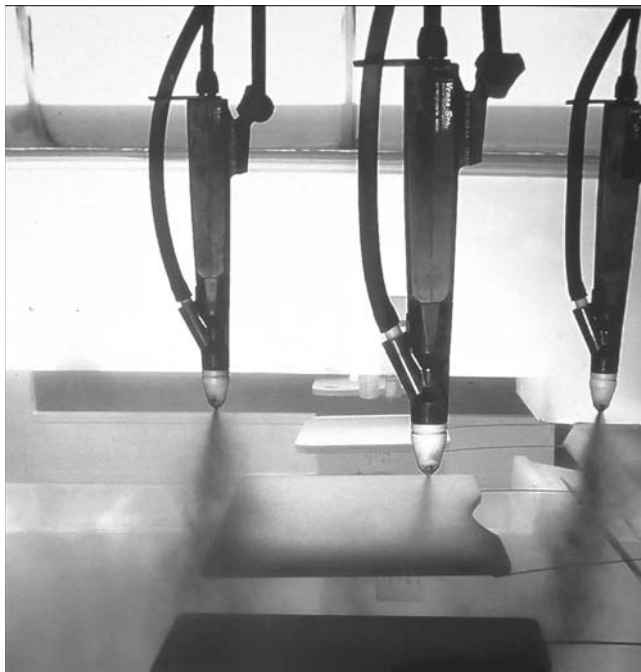
**FIGURE 7.16**
Application of UV curable powder onto MDF parts. (Courtesy of Nordson Corporation.)

used. IRM (medium-wave infrared radiation) is preferred because it efficiently heats the surface without the rise in the core temperature of the part. Surface temperatures are usually in the range of 100 to 120°C (212 to 250°F). A typical melting process cycle is approximately 3 min, depending on the nature of the substrate.

An example of a line for curing UV powders is shown in Figure 7.17.

### 7.7.4   Substrates Suitable for UV Powder Coating

Although UV powder coatings can be applied to a variety of substrates, including metals and plastics with high melting temperatures, their primary advantage is for coating of substrates, which are:[47]

- Temperature-sensitive materials
- Preassembled components
- Dense materials with highly pronounced heat sink characteristics

*Plastics*: Several types of plastics, such as polystyrene, high density polyethylene (HDPE), acrylonitrile butadiene styrene (ABS), resin/
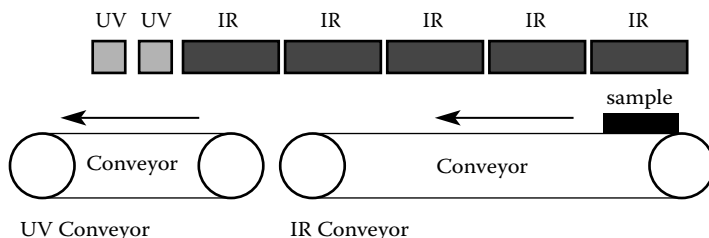
**FIGURE 7.17**
Principle of curing UV powder coating.

polybutylene terephthalate (PBT), polyamide, polycarbonate, and polypropylene oxide.

*Wood and wood composites*: Solid wood as well as particleboard and medium-density fiberboard (MDF) are suitable substrates for powder coating. They tend to emit volatiles such as entrapped air and moisture, and therefore require curing temperatures below 100°C (212°F) and preferably not higher than 80°C (144°F). A typical curing procedure for MDF is in Table 7.8.

*Preassembled parts*: Preassembled parts may contain components made from heat-sensitive substrates (e.g., plastic inserts, wiring). In contrast to the conventional method, where individual components are coated prior to assembly to avoid heat damage, UV powder coating permits the manufacturer to fully assemble a part prior to coating.

*Large-mass parts*: Conventional coating of large-mass parts requires exceedingly long times in convection ovens. A considerable reduction of times required for cure is to melt the powder with IR and use fast UV-initiated free radical curing reactions.

**TABLE 7.8**

Typical Curing Conditions for UV Powder Coatings on MDF

| Process Variable | Type of Coating | | Note |
|---|---|---|---|
| | **Clear** | **Pigmented** | **Note** |
| Melt temperature, °C | 100–120 | 100–120 | Medium-wave IR, |
| °F | 212–250 | 212–250 | convection or combination ovens |
| Melt time, s | 120 | 120 | Typical conditions |
| Type of UV lamp | Mercury | Gallium-doped mercury | Microwave or arc lamps |
| UV dose, mJ/cm$^2$ | 1,000 | 1,500–4,000 | Light bug IL-390 |

*Source:* Bayards, R., et al., *RadTech Report*, 15, No. 5, RadTech International N.A., p. 15 (2001). With permission from RadTech International N.A.

### 7.7.5 Industrial Applications

The first commercial application was the coating of a fully assembled electric motor.[48] The motor is assembled from parts of different sizes and thickness. Conventional powder coating flows and cures easily on thin and small parts, but the heavier parts may not ever reach the required melting temperature or cure completely even after extended periods of time. This technology is readily applicable to other products, such as wooden furniture with metal hardware.

Currently, the UV powder coating technology is used on a large scale for the following products:[49–53]

- MDF boards for furniture applications
- Preassembled metal objects containing heat-sensitive parts
- PVC flooring

Other applications include:[38,54,55]

- Aluminum wheels
- Automotive accessories (hatchback door closers, hydraulic shock absorbers, headlamp lenses, trim pieces, etc.)
- Electric motors
- Gas cylinders
- Hydraulic door closers
- Heavy-gauge parts
- Carbon-fiber-reinforced composites

## 7.8 Other Applications for UV Curing

### 7.8.1 Electronics

Electronics is a major application area for UV curing. Radiation curable resins for resists are the backbone of the imaging process to create electronic circuitry (see Section 7.5), but are also widely used as conformal coatings in the encapsulation of electronic components. In the latter application, UV curable adhesives are used to assemble the components,[56] and UV curable coatings are applied over the assembly to protect it from the environment. Epoxy resins appear to be the most widely used materials,[57–59] with silica-filled epoxies also being important.[60] Epoxy vinyl esters with high silica loading (up to 60 wt.%) are also promising because of their fast cure rate and physical properties, akin to the resins currently in use.[61] Fluorinated silicones, acrylated siloxanes, and cyanates have also been used successfully.[56] In order to ensure cure in the shaded areas, dual-curing systems are often used. A secondary

cure system, such as moisture, thermal, or oxidative, is used to augment the radiation energy cure.

Smart cards in the form of SIM cards for mobile (cell) telephones contain chip modules, and UV radiation curable epoxies have been shown to offer advantages in the encapsulation of these vital components.[62]

## 7.8.2 Optical Components and Optoelectronic Applications

### 7.8.2.1 Optical Fibers

Optical fibers are widely used in the telecommunication industry for the transmission of digital pulses of voice, video, and data. In order to keep losses in signal strength at a minimum, the fiber (usually a doped silica glass) has to be coated with a material of lower refractive index than its own refractive index. This layer is protected by a "buffer," which acts as a cushion. The buffer is encased in one or more protective layers (see Figure 7.18).[63] Both the primary and protective coatings are very often UV radiation curable.

Since the optical fibers are placed into locations that are difficult to access, the coatings are expected to last over 20 years. Tests indicated that UV cured protective coatings would be mechanically stable up to 100 years under ambient conditions.[64] Radiation curable adhesives can also be used for end-to-end splicing, termination of bundles, construction of optical sensors, and other areas in the optical field.[65]

### 7.8.2.2 Other Optical and Optoelectronic Applications

Radiation curing is an important part in the manufacture of compact disks and digital versatile disks (DVDs).[66] In the production of *compact disks* the replication and formation of the protective coat may be carried out with the use of UV curing.[67] The coatings are commonly based on methacrylates.

All *digital versatile disks* are made by cementing two disks together with a clear, UV curable adhesive.[66] The light required has to pass through one of the disks, and consequently, the choice of an initiator having the right absorption properties and of the type of lamp with sufficient power are of great importance.[68]
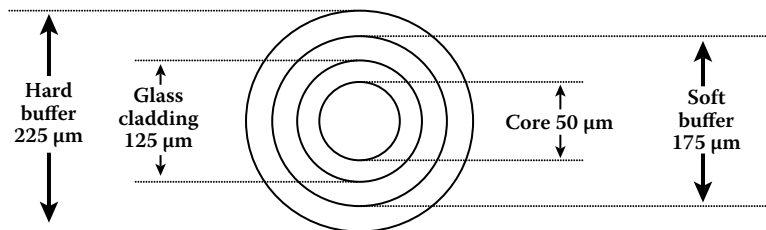


**FIGURE 7.18**

Schematic of the cross section of an optical fiber. (Davidson, R. S., *Exploring the Science, Technology and Applications of U.V. and E.B. Curing,* SITA Technology Ltd., p. 249 (1999). With permission from SITA Technology Ltd.)

Other applications are in the manufacture of optical lenses,[69] holograms,[70] and multilayer organic light-emitting devices.[71]

## 7.9 Automotive Applications

### 7.9.1 OEM Applications

A considerable amount of work has been done to develop a UV curable system of coatings for OEM applications. The basic requirement is that binders and reactive monomers have excellent weathering resistance. In many specific applications of pure UV curing systems, even in the case of clear coats, surface cracks occurred, depending on curing and storage conditions after curing, due to the volume shrinkage gradient, especially on black and dark base coats. Another shortcoming of pure UV curable systems is the occurrence of shadow areas with a lower state of cure.[72] The solution proposed was a dual-curing system that would include a second cross-linking chemistry, such as OH-functional resins like acrylic acrylates with conventional cross-linkers, e.g., isocyanates or acrylates, with NCO functionality or conventional curing systems, such as one-pack alkyd melamine.[72]

In spite of all the efforts mentioned above, no cases of wide application of UV/EB technology are known at this writing. As pointed out earlier, there are many difficulties to do that. The main issues the automotive industry is facing when considering this technology are:[73]

- Standard UV equipment and clear coats cannot ensure curing of coating in the shadowed areas.
- The use of high-intensity, short-wavelength UV lamps, which are known to cure clear coats in seconds, raises concerns about worker safety.
- Many of the clear coats that would be possibly suitable for coating and curing entire vehicle bodies contain free isocyanates and would not be accepted in an assembly line due to health and safety concerns.

On the other hand, there are many potential advantages of using UV or EB technology, such as substantial reduction of energy consumption, $CO_2$ production, and VOC emissions.

There are great efforts to develop not only clear coats, but also primers and base coats that would be curable by UV or EB.[73] The current approaches to UV/EB technology are:

- Clear coats without isocyanates
- Cationic and photolatent base clear coat formulations curing in shadowed areas

- The use of a plasma chamber that creates a diffuse light reaching all parts of painted vehicle[73]
- Cure by electron beam; could apply to primers, base coat, and clear coat

Even if all the chemistry and technology issues were solved, there would still be questions about the size of the equipment, nitrogen blanketing, and safety measures.

Other automotive applications involve electronic or electrical parts, such as sensor switch encapsulants; conductive inks for the rear-window defroster; motor balancing compounds; windshield wiper motor sealing adhesives; component-marking inks; tacking adhesives; screen-printed membrane switches; headlamps using special UV curing adhesives or conformal coatings; metallization prime coat; lens reflector adhesive (see Sections 7.2 and 7.8.1) and protective hard coats[74]; wheels, motors, and other using UV curable powders (Section 7.7.5); and tail lens assemblies.

One of the lesser known automotive applications is the use of clear coat over molded-in-color body side moldings. The coating has to be very tough and flexible to maintain adhesion without cracking from objects striking the molding. The advantages of UV coatings in this application are the speed of cure (small process footprint) and superior performance properties.[75]

Sheet molding compound (SMC) is a composite material that has been used as an alternative to steel for more than 30 years. SMC consists of a glass-fiber-filled unsaturated polyester and vinyl ester resin that has been compacted into a sheet.[76] These sheets are then placed into compression molds and formed into body panels, and these panels are then coated mainly by dual-cure coatings.[77]

Other possible applications are clear coats in automotive interiors (dashboard instrument screen-printed and top coats for gloss control, interior vinyl clear coat with excellent mar resistance and low gloss, wood grain printing and top coats for interior laminates), on alloy wheels and wheel covers and under the hood parts,[78] and UV curable paint over physical vapor deposition (PVD) surfaces of various parts.[79] Other examples are:

- Graphics and identifications (deep cure automotive name plates, manufacturers' logos on glass, battery labels, screen-printed oil filter housings, screen-printed windshield washer instructions etc.)
- Miscellaneous functional applications (black UV coatings for automobile windows, door handle gaskets, UV sealant for airbag explosive cartridges, abrasion-resistant top coat for metallized plastics, sealers and top coat for customized van and RV wood components, and more)

### 7.9.2 Automotive Refinish Applications

UV curing of automotive refinish coatings represents a powerful tool providing a fast curing process and improving the productivity of paint shops. The

development of a UV curing refinish primer system has been an important part of the technology. The other important factor has been the equipment based on flashlight technology. This equipment (a xenon lamp) generates UV flashes within a very short time interval with high energy.[72] Also, a homogeneous UV light distribution is realized to cure three-dimensional objects. This procedure is particularly useful for spot repairs with a cure time of less than 60 s. In automotive refinish applications the typical buildup of the paint layers comprises a putty, primer, base coat, and clear coat, depending on the type and extent of the body damage. In comparison with two-component (2K) urethane and epoxy systems, the UV materials cure considerably faster, and being only one-component coatings, they are ready to use and have practically an unlimited pot life. Moreover the UV curable primer system can be formulated with much higher solids, i.e., with a considerably lower VOC content,[80] which allows it be compliant with some of the most stringent local VOC regulations. Because of the low VOC content, the risk of encountering pop and gloss dieback is minimal. Additional advantages of UV curable systems are energy savings, because UV lamps consume a fraction of the energy required for forced-air baking, and the products are safe to use when following the recommended safety precautions as specified by the product manufacturers.[81,82]

## 7.10  Production of Composites by UV Radiation

### 7.10.1  Dental Applications

UV radiation curable dental compositions have been used since the early 1970s.[83,84] They consist of photocurable resins with silica filler and offer many advantages: they are ready for use on demand, offer an extended working time, and have an absence of air bubbles, a high polymerization rate, and good color stability. The silica filler provides mechanical strength and reduces shrinkage. However, the formulations have to meet several stringent requirements: The use of light with a wavelength shorter than 330 nm is unacceptable, since it may cause tissue damage and requires that the patient and the operator wear special protective wear. Therefore, photoinitiators for longer wavelengths are used (e.g., camphorquinone).[84] The material should be polishable, opaque to x-rays, and stable toward saliva, beverages, etc. Methacrylates are used as the base resin, in spite of their slow cure rate when compared to acrylates, which are less favorable because of their toxicological properties.

*Fissure sealants* are clear, low-viscosity, photocurable liquids, based on a mixture of tetrafunctional and difunctional methacrylates. Other dental photocurable materials are cements, adhesives, and denture base resins.[85–87]

*Glas-ionomer cements* are acid-based materials (using, e.g., polyacrylic acid), whose setting reaction involves neutralization of the acid groups by powdered solid bases (calcium fluoro-aluminosilicate glasses). Resin-modified glass ionomer cements are hybrid materials prepared by the incorporation of polymerizable components such as 2-hydroxyethyl methacrylate.[88]

## 7.10.2 Other Composite Applications

UV curing is used in several specialized applications in composite materials. Most of the radiation curable composite materials are processed by electron beam or microwave energy, mainly because of difficulties of getting the irradiating light to penetrate thick sections containing particles or fibers, which are often opaque to light.[89] The examples of UV cured composite materials include cure of glass and other fibers impregnated by photocurable resins in the production of coated filaments and in the production of prepreg sheets for waterproofing buildings and in filament winding.[90] Resin, containing carbon fibers were reported to be cured with UV light.[91] Recent developments are featured in Chapter 11.

## 7.11 Hydrogels

Hydrogels are three-dimensional, cross-linked hydrophilic polymeric structures able to absorb large quantities of water. They are synthesized by polymerization of hydrophilic monomers. The extent of the reversible swelling and deswelling property of these materials is known to depend on the nature of both intermolecular and intramolecular cross-linking, as well as the degree of hydrogen bonding in the polymer network. Hydrogels are mainly produced by the use of radiation processes, both UV and EB (more in Section 8.5.6). An example of a mature technology of this kind is the production of hydrogel wound dressings, highly absorbent diapers, contact lenses, and similar articles now being produced on a large scale; emerging applications include a hydrogel-based system for anticancer therapy due to local drug delivery and a variety of other medical applications.

Polyurethane hydrogels derived from UV curable urethane prepolymer and hydrophilic monomers were prepared and their properties were evaluated. The urethane prepolymer used in this study contained well-defined hard segments centered with a polyether-based soft segment and end-capped with methacrylate groups. The hydrophilic monomers studied were 2-hydroxyethyl methacrylate (HEMA), *N*-vinyl pyrrolidone, and glycerol methacrylate. Methacryloxypropyl tris(trimethysiloxy) silane (TRIS) was also used in some cases to modify properties. All compositions were UV

cured and formed hydrogels after hydration. The oxygen permeabilities of the hydrogels decreased as the water contents increased, and increased as the TRIS content was increased. The tear strengths and moduli decreased as the water contents of the hydrogels increased. Most compositions studied have higher oxygen permeability and tear strength than poly(HEMA) because of the presence of urethane prepolymer in the composition. The hydrogels are used for a variety of biomedical applications.[92]

Poly(*N*-vinyl-2-pyrrolidone) (PVP) hydrogels produced by high-energy radiation rely on water radiolysis as a primary process leading to cross-links. Conversely, ultraviolet direct irradiation into PVP leads to cross-linking through pyrrolidinone moiety photolysis. However, this process showed to be rather inefficient. However, cross-linking of PVP based on hydrogen peroxide photolysis, therefore mimicking water radiolysis, using UVC (e.g., low-pressure Hg lamp) or UVA radiation sources, is more efficient. The process efficiency and the properties of the hydrogel formed are discussed and compared with those of other methods of hydrogel production. Hydrogels based on PVP prepared by this method find use in biomedical applications.[93]

## References

1. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. I, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 159 (1998).
2. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. I, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 169 (1998).
3. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. I, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 171 (1998).
4. Stranges, A., *Proceedings RadTech '94 North America*, p. 415 (1994).
5. Jones, D. T., *Proceedings RadTech '94 North America*, p. 417 (1994).
6. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. I, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 173 (1998).
7. *Modern Coating and Drying Technology* (Cohen, E. D., and Gutoff, E. B., Eds.), VCH, Weinheim (1992).
8. Zimmerman, T., *Proceedings RadTech Europe '93*, p. 698 (1993).
9. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. I, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 184 (1998).
10. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. I, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 187 (1998).

11. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. I, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 189 (1998).

12. Roesch, K. F., *Proceedings RadTech Europe '93*, p. 940 (1993).

13. Garratt, P. G., *Proceedings RadTech Europe '87*, p. 10 (1987).

14. Roth, A., and Honig, M., *Proceedings RadTech North America '98*, p. 112 (1998).

15. *UV/EB Primer: Inks, Coatings and Adhesives*, RadTech International North America, Bethesda, MD, p. 13 (1995).

16. Des Roches, S., *Adhesives & Sealants Industry*, 12, No. 6, August (2005).

17. Johnston, J., *Pressure-Sensitive Tapes: A Guide to Their Function, Design, Manufacture and Use*, Pressure Sensitive Tape Council, Northbrook, IL, (2003).

18. Benedek, I., *Pressure-Sensitive Adhesives and Applications*, 2nd ed., CRC Press, Boca Raton, FL (2004).

19. Des Roches, S., and Murphy, W., *Adhesives & Sealants Industry*, 13, No. 8, August, p. 26 (2006).

20. Huber, H., Anzures, E., and Aceveda, M., *RadTech Report*, 11, No. 2, March/April, p. 17 (1997).

21. Nunez, C., McMinn, G., and Vitas, J., *RadTech North America '94 Conference Proceedings*, p. 42 (1994).

22. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology & Equipment*, Vol. I, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 185 (1998).

23. Burga, R., *Proceedings RadTech Asia '97*, p. 192 (1997).

24. Girling, C., private communication.

25. Robins, G., in *Radiation Curing of Polymers* (Randell, D. R., Ed.), The Royal Society of Chemistry, London, p. 78 (1987).

26. Caza, M., *Proceedings of RadTech Europe '97*, p. 392 (1997).

27. *UV/EB Curing Primer: Inks, Coatings and Adhesives*, RadTech International North America, Bethesda, MD, p. 17 (1995).

28. Nigam, B., *FLEXO*, September, p. 8 (2001).

29. Rasmussen, M. P., *RadTech Report*, 13, No. 2, p. 8 (1998).

30. Soroka, W., *Fundamentals of Packaging Technology*, 2nd ed., Institute of Packaging Professionals, Herndon, VA (1999).

31. Duncan, D., in *RadTech Printer's Guide*, www.radtech.org, p. 65.

32. Roffey, C. G., *Photopolymerization of Surface Coatings*, John Wiley & Sons Ltd., Chichester (1998).

33. *Stereolithography (SLA)*, Tech, Inc., www.techok.com/sla (2000).

34. Narey, B., *Conference Proceedings, Innovation in Plastics: Plastics Technologies for a Global Competitive Edge*, Rochester, NY, September 18–19, Paper J.012 (1990).

35. Koleske, J. V., *Radiation Curing of Coatings*, ASTM International, West Conshohocken, PA, p. 216 (2002).

36. Popat, A. H., and Lawson, J. R., U.S. Patent 6,025,114 to Zeneca Ltd. (2000).

37. Yamamura, T. et al., U.S. Patent 5,981,616 to DSM, NV, JSR Corporation, Japan Fine Coatings Co. Ltd. (1999).

38. Mills, P., *RadTech Report*, 11, No. 6, November/December, p. 16 (1997).

39. Mills, P., Blatter, W., Binder, J., and Mitchell, S., *UV Powder Application Guide*, RadTech International North America, Chevy Chase, MD, Chapter 1, p. 6 (2002).

40. Witte, F. M., de Jong, E. S., and Misev, T. A., *RadTech Report*, 10, No. 5, September/October, p. 14 (1996).

41. Zahora, E. P., et al., *Modern Paint and Coatings*, October, p. 120 (1994).
42. Witte, F. M., et al., *RadTech Europe 1995, Conference Proceedings*, Maastricht, p. 437 (1995).
43. Finter, J., Frischinger, I., Haug, Th., and Marton, R., *RadTech Europe '97 Conference Proceedings*, Lyon, France, p. 489 (1997).
44. Gottschling, P., and Stachyra, Z., *RadTech Report*, 13, No. 4, July/August, p. 42 (1999).
45. Mills, P., *UV Powder Application Guide*, RadTech International North America, Chevy Chase, MD, Chapter 3, p. 15 (2002).
46. Mihalic, S. D., and Mills, P., *RadTech Report*, 13, No. 4, July/August, p. 26 (1999).
47. Drummond, K. C., and Guskov, S. V., *RadTech Report*, 13, No. 4, July/August, p. 22 (1999).
48. Mills, P., *RadTech Report*, 13, No. 4, July/August, p. 31 (1999).
49. Buysens, K., and Hammerton, D. A., *RadTech Report*, 13, No. 4, July/August, p. 18 (1999).
50. Buysens, K., and Jacques, K., *Eur. Coatings J.*, 9, p. 22 (2001).
51. Bayards, R., et al., *RadTech Report*, 15, No. 5, September/October, p. 15 (2001).
52. Heathcote, J., *RadTech Report*, 15, No. 5, September/October, p. 10 (2001).
53. Karlsson, L., and Leach, C., *Industrial Paint & Powder*, 78, No. 4, April, p. 12 (2002).
54. Mills, P., *RadTech Report*, 15, No. 5, September/October, p. 32 (2001).
55. McFadden, B., *RadTech Report*, 11, No. 1, January/February, p. 15 (1997).
56. Davidson, R. S., *Radiation Curing, RAPRA Review Reports*, 12, No. 4, p. 24 (2001).
57. Bittmann, E., and Ehrenstein, G. W., *Plaste u. Kautschuk*, 41, No. 5, September, p. 216 (1994).
58. Bittmann, E., and Ehrenstein, G. W., *ANTEC '96, Conference Proceedings*, Vol. II, Indianapolis, IN, May 5–10, p. 1465 (1996).
59. Sheehan, J., *Pitture e Vernici*, 71, No. 18, November, p. 26 (1995). In Italian and English.
60. Stampfer, S., and Ehrenstein, G. W., *ANTEC '98, Conference Proceedings*, Vol. II, April 26–30, p. 1173 (1998).
61. Baikerikar, K. K., et al., *Conference Proceedings, RadTech North America '98*, p. 712 (1998).
62. Most, R., *European Design Engineer*, April, p. 58 (2000).
63. Davidson, R. S., *Radiation Curing, RAPRA Review Reports*, 12, No. 4, p. 18 (2001).
64. Cutler Jr., O. R., *RadCure '84*, Technical Paper FC84-1022, Atlanta, GA, September 10–13 (1984).
65. Murray, R. T., and Jones, M. E., *Command Cure Precision Cements in Optics*, Technical Information Brochure, ICI Resins-US (1993).
66. Ledwith, A., in *Photochemistry and Polymeric Systems* (Kelly, J. M., et al., Eds.), Royal Society of Chemistry, Cambridge, UK, p. 1 (1993).
67. Kitans, R., and Amo, M., EP 962301 to Kitano Engineering Co. Ltd. (1990).
68. Skinner, D., *Proceedings RadTech North America '98*, Chicago, IL, p. 140 (1998).
69. Luetke, S., *RadTech Report*, 10, No. 2, March/April, p. 29 (1996).
70. Sponsler, M. B., *The Spectrum*, 13, p. 7 (2000).
71. Braig, T., et al., *Conference Proceedings, ACS Polymeric Materials Science and Engineering*, Vol. 80, Anaheim, CA, Spring, p. 122 (1999).
72. Maag, K., Lenhard, W., and Löffler, H., *Prog. Org. Coat.*, 40, p. 93 (2000).
73. Seubert, C. M., and Nichols, M. E., *RadTech Report*, 22, No. 6, November/December, p. 27 (2008).

74. Slocum, S., and Mordhorst, S., *Radtech Report*, 22, No. 6, November/December, p. 40 (2008).
75. Joesel, K., *Product Finishing—UV Coating Technology Supplement*, p. 16s (2004).
76. Mallick, P. K., in *Composite Materials Technology* (Mallick, P. K., and Newman, S., Eds.), Hanser Publishers, Munich, 1990, p. 27.
77. Joesel, K., *Product Finishing—UV Coating Technology Supplement*, p. 18s (2004).
78. Joesel, K., *Product Finishing—UV Coating Technology Supplement*, p. 21s (2004).
79. De Stephani, J., *Product Finishings*, August (2009).
80. Stropp, J. P., et al., *Progr. Org. Coat.*, 55, p. 29 (2006).
81. *UV Cure Automotive Refinishing Products*, RadTech International North America, www.radtech.org.
82. *BodyShop Business*, May (2005).
83. Linden, L.-A., in *Radiation Curing in Polymer Science and Technology*, Vol. IV (Fouassier, J. P., and Rabek, J. F., Eds.), Elsevier Applied Science, London, p. 387 (1993).
84. Anon., *Revista de Plasticos Modernos*, 78, No. 519, September, p. 287 (1999). In Spanish.
85. Woods, J. G., in *Radiation Science and Technology* (Pappas, S. P., Ed.), Plenum Press, New York, Chapter 9, p. 333 (1992).
86. Linden, L. A., in *Polymeric Materials Encyclopedia* (Salamone, J. C., Ed.), CRC Press, Boca Raton, FL, p. 1839 (1996).
87. Andrzejewska, E., private communication.
88. Andrzejewska, E., Andrzejewski, M., Socha, E., Zych-Tomkowiak, D., *Dental Mater.*, 19, p. 501 (2003).
89. Davidson, R. S., *Radiation Curing, RAPRA Review Reports*, 12, No. 4, Rapra Technology Ltd., p. 19 (2001).
90. Graff, G., *Modern Plastics International*, 26, No. 9, September, p. 38 (1996).
91. Muranaka, K., U.S. Patent 5, 591,784 to Three Bond Co. Ltd. (1997).
92. Lai, Y.-C., and Baccei, L. J., *J. Appl. Polym. Sci.*, 42, p. 3173 (1991).
93. Fechine, G. J. M., Barros, J. A. G., and Catalani, L. H., *Polymer*, 46, p. 283 (2005).

# 8

## *Applications of Electron Beam Radiation*

The chemical reactions of monomers, oligomers, and significant changes in properties of polymers induced by ionizing radiation discussed in previous chapters can be used for a variety of practical applications. Besides the already mentioned advantages in clean and safe technology, the almost instant conversion and excellent control of dosage and penetration depth electron beam processing found its way to a variety of industrial applications, such as wire and cable insulations; tire manufacturing; production of polymeric foams, heat-shrinkable films, and tubings; curing of coatings, adhesives, and composites; as well as printing. Large-scale industrial applications of ionizing radiation started in the late 1950s, when Raychem introduced the production of polyethylene heat-shrinkable tubing and W. R. Grace started to manufacture polyolefin packaging. At about the same time Goodyear and Firestone initiated investigation of modification of rubber compounds by electron beam irradiation for tire applications.[1]

The equipment used must be matched to the given process. For example, for wire and cable, as well as for precuring of tire components and processing of rubber products, and polyolefin foams, where greater electron penetration is required, accelerators with energies ranging from 0.5 to 5 MeV and power rating less than 200 kW are used.[2] Coatings, adhesives, printing, and thin films can be processed by low-energy accelerators with energies typically in the 100–500 keV range. Some of the major industrial applications using electron beam processing of polymeric systems are in Table 8.1.

## 8.1 Electron Beam Process in Wire and Cable Technology

More than 30% of the industrial electron beam processors in the world are used in the radiation cross-linking of wire and cable insulation,[3] and this application is growing.

The largest volume of polymeric materials used for wire and cable insulation are thermoplastics, namely, polyethylene (PE) and polyvinylchloride (PVC),[4] and to a lesser degree elastomeric compounds. The main reason for the prevalence of PE and PVC in wire and cable insulation is their easy processing and relatively

**TABLE 8.1**

Major Commercial Applications of Electron Beam Processing of Polymeric Materials

| Material/Substrate | Application | EB Process |
|---|---|---|
| Polyolefins and polyvinylchloride, some elastomers | Wire and cable insulation | Cross-linking, 0.4–3 MeV, at approx. 10 kGy or higher |
| Elastomers | Tire manufacture, improved green strength of components and tire performance | Cross-linking with high-energy electrons |
| Polyolefins and PVC | Improving thermal stability, uniformity, and fine structure for packaging and insulation, rubber sheeting | Cross-linking with high-energy electrons |
| Wood impregnated with acrylic and methacrylic monomers | No-wear high-performance floors for high-traffic areas | Polymerization by electron beam |
| Polyolefins | Heat-shrink films and tubing | Cross-linking |
| Polymeric films, metallic foils, paper, metal, wood | Curing of adhesives, coatings, and inks | Low energy processing in the 100–500 keV range at 0.1–0.2 MGy |
| Polytetrafluoroethylene | Degradation into low-molecular-weight products ("micropowders") used as additives to coatings, lubricants, and inks | High-energy irradiation at 200–400 kGy |

low cost. However, their main disadvantage is that their physical properties, such as plastic flow at elevated temperatures, environmental stress cracking, poor solvent resistance, and low softening temperatures,[3] cannot always meet demands imposed on them by modern applications. Cross-linking of these materials improves their toughness, flexibility, and impact resistance, resistance to solvents and chemicals, as well as their service temperature.[5,6]

There are essentially three cross-linking processes used in the wire and cable industry. Two kinds of chemical cross-linking, employing organic peroxides or silanes, respectively, are still frequently used for the improvement of PE and other polymer-based insulations for wire and cable.[7,8] However, the advantages of radiation cross-linking over the chemical process have brought about its steady growth of about 10–15% annually[9] since the mid-1970s, when high-energy and high-current electron accelerators became widely available for radiation processing.[10,11]

The most common compound for peroxide cross-linking of PE in the wire and cable industry is dicumyl peroxide (DCP), which decomposes at 120–125°C (248–257°F), generating free radicals needed for the process plus by-products (carbinol, acetophenone, and methane).[7] The production line for continuous vulcanization of wire and cables by peroxide must be about 200 m (61 ft) long.[12] The plant space required for radiation cross-linking using

**TABLE 8.2**

Comparison of Radiation and Peroxide Cross-Linking of Wire and Cable Insulation Materials

| Property | Radiation Cross-Linking | Peroxide Cross-Linking |
|---|---|---|
| Energy consumption | Low | High |
| Line speed, m/min (ft/min) | Fast, up to 500 (1,640) | Slow, max. 200 (655) |
| Processing | Off-line | On-line |
| Factory space | Relatively small | Relatively large |
| Product sizes | Wide variety | Fixed |
| Process control | Current and line speed | Heat flow |
| Insulation materials[a] | LDPE, FRLDPE, HDPE, FRHDPE, PVC | LDPE |
| Maintenance cost | Low | High |
| Start-up | No scrap | 100 m (330 ft) scrap at start |
| Voltage rating, kV | Up to 5 | 50 |
| Capital cost | High | Moderate |

[a] LDPE = low-density polyethylene, FRLDPE = flame-retardant LDPE, HDPE = high-density polyethylene, FRHDPE = flame-retardant HDPE, PVC = polyvinylchloride.

electron accelerators is considerably smaller. Moreover, energy consumption for the radiation process is much lower than that for the chemical cross-linking process.[13] As pointed out earlier, the dose required for the desirable degree of cross-linking is determined by the electron current of the accelerator and by the wire or cable speed; therefore, the process control is quite simple.[14] Depending on the source (most commonly steam) and the size of the product, regulation of the temperature of the vulcanization line, typically in the range of 200–400°C (392–752°F), is more complicated than the control of the electron beam current. While chemical cross-linking is applicable only to polyethylene and elastomers, radiation can be used for the cross-linking of PE, PE with flame retardants, PVC, some fluoropolymers, and some elastomers. A comparison of peroxide and radiation cross-linking in the wire and cable applications is in Table 8.2.

The silane cross-linking of polyethylene has been used mainly in low-voltage applications. It is a two-stage process, and the curing time is dictated by the time required for the moisture to diffuse thoroughly into the insulation. Consequently, the process is rather slow. Another drawback of this system is the limited shelf life of the silane cross-linking agent and the significant cost of the compound.[15]

Polymeric materials used for electrical insulation have to exhibit not only good electrical properties, but also good mechanical properties and good appearance. In addition to reliable electrical performance, thermal stability is important, mainly for miniaturized electronic and electrical equipment. Long-term stability at temperatures in the range of 90–125°C (194–257°F) is

required. The short-term stability determines the resistance of the insulation to melted solder and its cut-through resistance.

The most important performance tests on insulating materials are those for dielectric strength and insulation resistance. Wire and cable products are required to perform over different voltage ranges and at different conditions, such as humid environment and after aging.[16] One of the tests is dielectric breakdown. Dielectric breakdown occurs when electrons detached from the molecule acquire sufficient energy in the electric field to yield secondary ionization and avalanche.[17] For most polymers, the dielectric strength can be as high as 1,000 MV/m. However, under practical conditions, breakdown of polymer insulation occurs at much lower electric field strengths. For example, if the power dissipated in the insulating material raises its temperature enough to cause a thermal stress, the dielectric breakdown occurs at a much lower field strength. Another factor is surface contamination, which can cause many polymeric insulators to break down by tracking on their surface.[18]

Two other important electrical properties must be taken into consideration when polymers are used as insulation for a high-voltage power cable[19] or electronic wires.[20] These are the dielectric constant and the dielectric loss factor, which characterize the energy dissipation in the insulation, the capacitance, the impedance, and the attenuation.

In contrast to metals and semiconductors, the valence electrons in polymers are localized in covalent bonds.[21] The small current that flows through polymers upon the application of an electric field arises mainly from structural defects and impurities. Additives, such as fillers, antioxidants, plasticizers, and processing aids of flame retardants, cause an increase of charge carriers, which results in a decrease of their volume resistivity.[22] In radiation cross-linking electrons may produce radiation defects in the material; the higher the absorbed dose, the greater the number of defects. As a result, the resistivity of a radiation cross-linked polymer may decrease.[23] Volume resistivities and dielectric constants of some polymers used as insulations are in Table 8.3. It can be seen that the values of dielectric constants of cross-linked polymers are slightly lower than those of polymers not cross-linked.

Abrasion resistance and solder iron resistances are two other important properties required from a wire and cable insulator. These properties are critical for polymers used as sheathing or jacketing for hookup wire. Cross-linking improves both of them.[24]

Cross-linkable polymers used for wire and cable insulations are polyolefins, certain fluoropolymers, and elastomers. Among these, radiation cross-linked polyethylene is the most widely used. The radiation cross-linking process of PE has also been the most widely studied.[25–28]

High-voltage PE insulation thicker than 4 mm (0.16 in.) tends to form voids due to heat accumulation, the evolution of hydrogen gas, and discharge breakdown due to accumulation of excess charges[29] when irradiated. To eliminate this problem, the addition of prorads (such as multifunctional

**TABLE 8.3**

Volume Resistivity and Dielectric Constant Values of Polymeric Insulating
Materials

| Insulating Material | Volume Resistivity, ohm.cm | Dielectric Constant | |
| --- | --- | --- | --- |
| | | Uncured | Cross-Linked |
| Low-density polyethylene | $10^{18}$ | 2.3 | 2.0 |
| High-density polyethylene | $10^{16}$ | NA | NA |
| Rigid PVC | $10^{16}$ | NA | NA |
| Plasticized PVC | $10^{11}$–$10^{14}$ | 3.8 | 3.2 |
| Polypropylene | $10^{16}$ | 2.3 | NA |
| EPDM | $10^{16}$ | 3.1 | 3.6 |

*Source:* *Radiation Processing of Polymers*, (Singh, A., and Silverman, J., Eds.) Carl Hanser
Publishers, p. 77 (1992). With permission of Carl Hanser Publishers.

acrylate and methacrylate monomers) to reduce required dose[30] is necessary.
Some monomers, such as triallyl cyanurate and dipropargyl succinate, are
effective in reducing the dose required for cross-linking, but they have an
adverse effect on the dissipation factor of the insulation.[31]

PVC, another widely used polymer for wire and cable insulation, cross-
links under irradiation in an inert atmosphere. When irradiated in air, scission
predominates.[32,33] To make cross-linking dominant, multifunctional mono-
mers, such as trifunctional acrylates and methacrylates, must be added.[34,35]

Fluoropolymers, such as copolymers of ethylene and tetrafluoroethylene
(ETFE), or polyvinylidene fluoride (PVDF) and polyvinyl fluoride (PVF), are
widely used in wire and cable insulations. They are relatively easy to process and
have excellent chemical and thermal resistance, but tend to creep, crack, and pos-
sess low mechanical stress at temperatures near their melting points. Radiation
has been found to improve their mechanical properties and crack resistance.[36]

Ethylene propylene rubber (EPR) has also been used for wire and cable
insulation. When blended with thermoplastic polyefins, such as low density
polyethylene (LDPE), its processibility improves significantly. The typical
addition of LDPE is 10%. Ethylene propylene copolymers and terpolymers
with high PE content can be cross-linked by irradiation.[34]

## 8.1.1 Equipment and Process

Radiation cross-linking of wire and cable insulation requires, in general,
medium-energy electrons in the range of 0.5 to 2.5 MeV. The electrostatic
electron beam systems using high DC voltage to accelerate electrons have
been found to be most suitable.[37] Cross-linking of wire and cable insulation
results from the dissipation of the energy carried by fast electrons penetrat-
ing into the insulation. As pointed out in Section 2.2, the depth of penetration

is governed by the accelerating voltage. For that reason, the equipment used has to have sufficient beam energy, since it defines the maximum thickness of the insulation, which can be penetrated and effectively cross-linked by the electrons.[38,39] The effective depth (optimum penetration) of the electron beam is defined as the thickness in which the exit plane dose equals the incident surface dose. The ratio of the peak dose to the entrance dose is defined as dose uniformity.[37] Because of the nature of the process,[40] the energy imparted to the insulating material is not uniformly distributed. However, the physical properties of the insulation modified by radiation cross-linking are not very sensitive to the variation of the dose in depth. Thus, the heterogeneity of the dose should not be of great concern, and the maximum-to-minimum-dose ratio of 1.5 or less is usually satisfactory.[37]

The volume resistivity of polyethylene is very high, and the electrons that come to rest in the insulation layer cannot be easily removed. Therefore, it is necessary for the electrons irradiating the wire or cable to penetrate through the insulation to ensure that no charge is accumulated in the wire or cable, causing dielectric breakdown.[41] PVC has a lower resistivity than PE; therefore, charges during the irradiation can leak from the insulation through the wire or cable conductor to ground. The penetration depth (or range of electrons) for a given electron beam depends on the thickness of the wire or cable insulation, and the diameter of the conductor can be calculated.[42,43] Usually, the penetration of twice the radial thickness of the insulation is sufficient.[43]

Irradiation cross-linking of small wires and cables with insulation thickness around 1 mm (0.040 in.) is done under a scanner. The wire or cable is strung between two drums to form a figure eight (see Figure 8.1) and is irradiated on both sides. The dose is controlled automatically by a servolink.

Cables with a large conductor cross section (e.g., 150 mm$^2$) and thicker insulation (2 mm or 0.080 in.) require a multiside irradiation.[43–45] An example of a four-sided irradiation using a single accelerator is in Figure 8.2,[45] where the scanning horn is placed over four wire/cable strands twisted between rollers. The cable speed, the rotation speed of the twisting cable, and the scanner frequency are coordinated by a servomechanism.[45] Some high-frequency accelerators can provide deflected electron beams capable of irradiating the cable from three directions. In such an arrangement, the required electron penetration equals the required thickness of insulation; consequently, electron accelerators of lower energy can be used.[45]

The doses required for electron beam cross-linking of PE and PVC (compounded with prorads) are 100–300 kGy and 40 kGy, respectively. The number of passes of wire or cable through the beam has its limitations, since sufficient spacing is required between passes to avoid overlap or shadows. The overall energy utilization coefficient can vary anywhere between 0.20 and 0.80.[46] Leading manufacturers of EB equipment provide formulas for the calculation of required energy[47] and processing rate for the given dimensions of a wire and cable.[47–50]
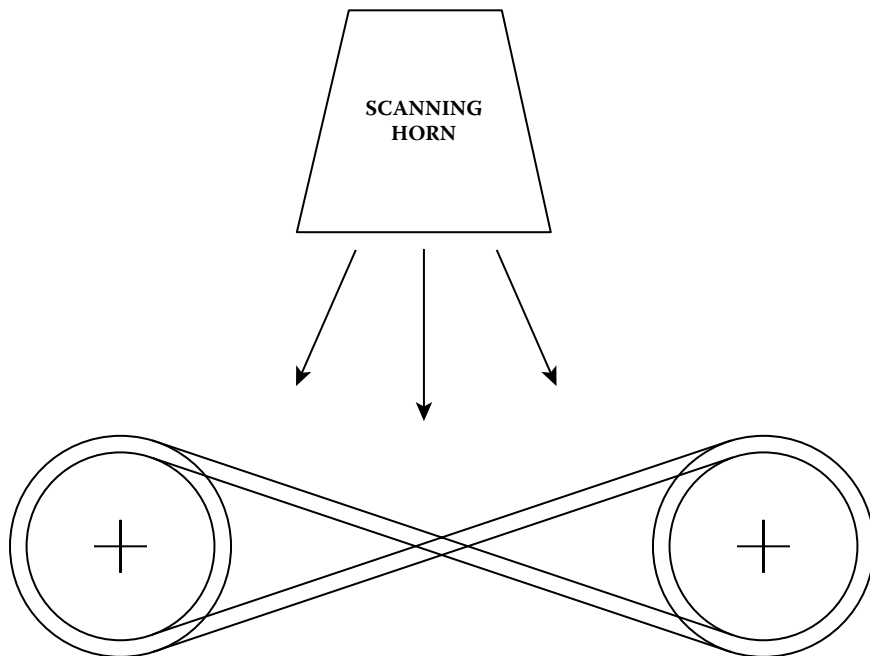
**FIGURE 8.1**
Two-sided irradiation of a wire by electron beam. (*Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Publishers, p. 82 (1992). With permission from Carl Hanser Publishers.)

## 8.1.2 Materials

Depending upon the end-use requirement, wire jacketing is most often made from formulated polyethylene. Blends of polyethylene and ethylene-propylene rubber are used if greater flexibility is needed, especially as the diameter of the jacketing increases as for cables. Another possibility is EPDM rubber with
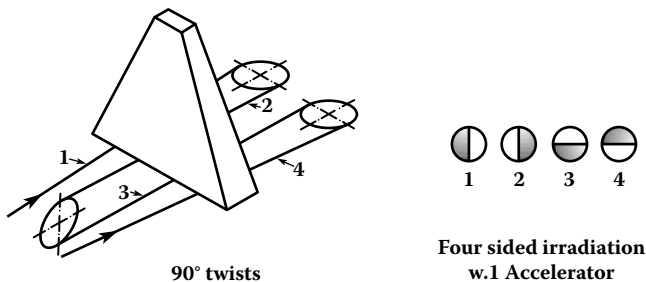


**FIGURE 8.2**
Four-sided irradiation of a wire. (*Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.) Carl Hanser Publishers, p. 84 (1992). With permission from Carl Hanser Publishers.)

**TABLE 8.4**

Example of an Electron Beam Curable Fire-Resistant Insulating Material

| Material | Amount (phr) |
|---|---|
| Vistalon EPDM with ENB | 100 |
| Hydrated aluminum oxide | 100 |
| Paraffinic process oil | 50 |
| Silane A 172 | 2 |
| Antioxidant | 1 |
| TMPT (75%) | 3 |
| Total | 256 |

*Source:* *Vulcanization of Vistalon Polymers*, ExxonMobil Chemical (2000).

*Note:* phr = parts per hundred parts of rubber, ENB = ethylene norbornene (curing site in the elastomer), TMPT = trimethylolpropane trimethacrylate (prorads).

ENB monomer. Table 8.4 presents a typical radiation cross-linkable jacketing formulation.[51]

Hydrated aluminum oxide is a preferred flame retardant that liberates its water of hydration when exposed to flames, in contrast to chlorinated materials, which give off toxic gases as by-products. The paraffin oil is a processing aid that enhances the ability to extrude such materials. The silane is a coupling agent that improves the interaction between the polymers and the aluminum trihydrate. Trimethylolpropane trimethacrylate (TMPT) enhances the radiation response.

When enhanced temperature resistance is required, polyvinylidene fluoride or other fluoropolymers are used.[52] Fluoropolymers have the advantage of being oil resistant and flame retardant, but are also more expensive base materials. PVDF is one of the materials that is very easy to cross-link by EB radiation.

## 8.1.3 Recent Developments and Trends

Radiation cross-linking of wire and cable insulations has been growing steadily over the past 33 years. On the weight bases, more wire insulation than cable insulation has been cross-linked by electron beams, with most of the wire being used in electronics. Recently, most of the growth was in flame-retardant insulations. Besides PE and PVC, chlorinated polyethylene and chlorosulfonated polyethylene (Hypalon®) have been used.[53] Polypropylene (PP), similar to PE in price but stronger, can also be cross-linked by electron beams, but requires prorads, such as trimethylolpropane triacrylate. These reduce the dose required for the cross-linking of PP considerably.[54] Another unique radiation cross-linked insulation is polymeric foam wire and cable insulation.[55]

## 8.2 Electron Beam Process in Tire Technology

A pneumatic tire is composed of several components, which must retain their shape and dimensions during the process of being built and during final vulcanization. Such components are inner liner, chafer strip, white sidewall, veneer strip, and body and tread ply skims or skim coats (see Figure 8.3).[56] When these various parts of a tire are partially cured by radiation, they will not thin out or become displaced during the construction of the tire, nor will they thin out and flow during the vulcanization in the mold, as would components that were not irradiated. In some cases, material reduction is possible and more synthetic rubber can be used in place of the more expensive natural rubber without a loss of strength.[56]

Body plies of a tire are various rubber-coated cord fabrics (see Figure 8.4). These are subjected to stresses when the tire is built. If a body ply does not have sufficient green (i.e., uncured) strength, the cords will push through the rubber coating (skim) during the building and vulcanization of the tire, resulting in irregular cord placement or defect in the tire. For example, damage can occur from turning the ply around the bead during the building of the tire when the skim compound does not have adequate green strength. Green strength may be defined as that level of cohesive strength that allows an essentially un-cross-linked polymer-based composition to deform uniformly, under stress, without sagging or nonuniform thinning (necking).

Tires are built most commonly on expandable drums. When the drum is expanded to shape the green (i.e., uncured) tire, the cord spacing in the
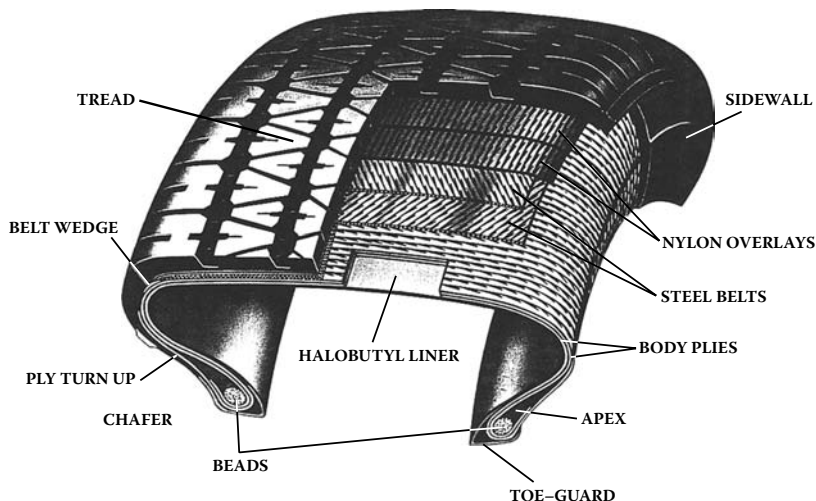


**FIGURE 8.3**
Cross section and components of a radial pneumatic tire.
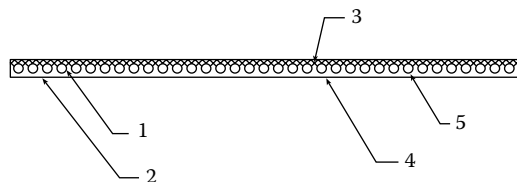
**FIGURE 8.4**
Cross section of a tire body ply with controlled depth of partial cross-linking. 1, reinforcing cord fabric; 2, skim coat; 3, partially cross-linked skim coat by electron beam; 4, building tack preserved; 5, bleed cord.

body plies must be maintained. In tread plies, correct cord placement must be maintained during the change in their angle occurring during the shaping in the vulcanization process. Thus, the tread ply skim compound, like the body skim compound, has to have adequate green strength. Another important property of the rubber material in the tire building is the building tack, which is essentially adhesion to itself (autohesion). The level of building tack is reduced with the degree of cross-linking of the rubber compound. Thus, the green strength and building tack must be in good balance (see Figure 8.6).

The construction of a tubeless tire starts with placing the inner liner on the building drum. Then the different plies and other components are added, including the tread, which is applied last. Then the tire is generally expanded into torroidal shape by air pressure. Additional expansion occurs in the heated curing mold during vulcanization of the tire. During the expansion of the green tire and vulcanization, the inner liner tends to decrease in thickness (thins out) and flow considerably, especially in the shoulder area, depending on the green strength of the inner liner compound. Since the inner liner has the function to maintain the inflation pressure of a tire during its service, its gauge is critical to the air permeation. Thus, maintaining its thickness in the curing process is very important. Normally, this is ensured by using a thicker inner liner than necessary. Partial cross-linking of the compound by irradiation makes this unnecessary, resulting in saving material and cost.

The degree of partial cure has to be precisely controlled, as pointed out earlier, in order to ensure sufficient green strength and sufficient building tack necessary for the construction of the tire. The electron beam process is ideally suited for that. The partial cure or precure is done by simply placing the tire components on a conveyor belt, which is passed under the electron beam source, and exposing them to the proper irradiation dose. The dose depends on the particular elastomer (or elastomer blends) and type and amount of fillers, oils, antioxidants, and other compounding ingredients that more or less affect the radiation response of the compound. Typically, a dose of 0.1 to 20.0 Mrad (1 to 200 kGy) is required.[56]

The effects of electron beam irradiation on the rubber compounds for tires can be readily evaluated by measuring green strength and recovery. Green strength is measured in a fashion similar to that of tensile strength: straight-sided specimens typically 12.5 mm (0.5 in.) wide and 2.5 mm (0.1 in.) thick are stretched by a tensile tester (e.g., Instron) and the peak stress or tensile strength is recorded. The laboratory test results from an uncured sheet can show whether the material has sufficient green strength for the given tire component if the slope of its tensile stress-strain curve remains positive beyond the maximum extension to which the component will be subjected before it is vulcanized.[56] For example, the green strength of the inner liner compound for a radial tire can be shown to be sufficient if the slope of its tensile stress-strain curve is positive throughout the 100 to 300% elongation range, because maximum extension of the inner liner during the forming of the tire falls into the lower end of this range. If extension in the crown section of the tire were to exceed the uniform deformation capability of the liner, nonuniform thinning would occur.[57]

The recovery may be evaluated by the conventional Williams plasticity test (ASTM D926), Procedure 2.2.1, at 100°C (212°F). Other tests may be used, although the ones mentioned here were found to correlate best with the behavior of the rubber compound and tire components during the building and vulcanization of the tire. Results from green strength and recovery tests from different compounds reported in Hunt and Alliger[56] are shown in Table 8.5, and green strength of irradiated ply skim stocks with different compositions in Table 8.6. Physical properties from vulcanized bromobutyl inner liner compound (unaged and aged) are in Tables 8.7A and 8.7B.

**TABLE 8.5**

Effect of Irradiation on Green Strength and Recovery of Different Tire Compounds

| Compound | Property | Dose, kGy | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | | 0 | 50 | 100 | 150 | 200 |
| Inner liner | Green strength, lb[a] | 3.0 | 15.3 | 20.0 | 22.9 | 33.8 |
| | Recovery, %[b] | 8.0 | 31.5 | 42.5 | 80.0 | — |
| Chafer strip | Green strength, lb[a] | 22.8 | 35.1 | 42.1 | 52.0 | 58.2 |
| | Recovery, %[b] | 9.0 | 39.0 | 48.0 | 54.0 | — |
| White sidewall | Green strength, lb[a] | 8.2 | 17.6 | 20.0 | 21.2 | — |
| | Recovery, %[b] | 10.0 | 35.5 | 113.5 | 110.0 | — |
| Veneer strip | Green strength, lb[a] | 13.0 | 17.5 | 21.7 | 26.0 | — |
| | Recovery, %[b] | 10.5 | 35.5 | 71.0 | 118.5 | — |

[a] Peak value in tensile test.
[b] Plasticity. Williams (ASTM D928, Procedure 2.2.1).

**TABLE 8.6**

Green Strength of Irradiated Ply Skim Stocks with Different Elastomer
Compositions (lb)

| Type of Skim Stock | Nominal Radiation Dose, kGy | | | | |
|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 50 |
| NR/solution SBR 50/50 | 3.2 | 4.6 | 6.6 | 8.5 | 11.3 |
| 100% solution SBR | 0.6 | 0.8 | 1.7 | 3.2 | — |
| SBR/BR 75/25 | 1.5 | — | — | — | 25.7 |
| 100% BR | 3.5 | 8.5 | 13.6 | 18.2 | — |
| 100% SBR | 0.4 | 2.0 | 5.8 | 9.4 | — |

*Source:* Mohammed, S. A. H. and Walker, J. *Rubb. Chem. Technol.* 59: 3, p. 494. (With permission
from Rubber Division ACS.)

The irradiated components can be placed adjacent to sulfur-containing
unvulcanized elastomeric compounds and, when necessary, coated with
suitable adhesive between the contacting surfaces to ensure good bond after
final cure of the tire.[56]

The equipment and technology have developed significantly over the past
two decades the high-energy electron beam process has been in use. The origi-
nal equipment was shielded by concrete vaults, which were 70 to 80 ft long,
35 to 40 ft high, and 16 to 20 ft wide. The walls of the treatment area might have
been 4–6 ft thick. Pay-off and take-up equipment would add another 60 to 80 ft
to the overall length of the system. The tire parts were treated almost exclu-
sively off-line.[55–57] Due to a strong push by tire manufacturers to make the
equipment more user-friendly, the accelerators were redesigned to produce
radiation in the forward direction, which required radiation shielding only in
the front and on sides.[56] Furthermore, the vault was placed below the ground

**TABLE 8.7A**

Physical Properties from Vulcanized Bromobutyl Inner Liner Compound (Unaged)

| Property | Nominal Radiation Dose, kGy | | | | |
|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 50 |
| Hardness, durometer A | 53 | 50 | 48 | 46 | 46 |
| 100% modulus, MPa | 1.2 | 1.1 | 1.0 | 0.8 | 0.9 |
| 300% modulus, MPa | 4.8 | 4.3 | 4.3 | 3.6 | 4.0 |
| Tensile strength, MPa | 9.9 | 8.7 | 8.0 | 6.9 | 7.5 |
| Elongation at break, % | 640 | 600 | 610 | 670 | 620 |
| Peel adhesion at RT, kN/m | 4.2 | 3.2 | 6.4 | 3.8 | 3.6 |
| Peel adhesion at 100°C, kN/m | 6.3 | 3.7 | 3.9 | 1.1 | 1.4 |
| Fatigue, kGy (cured to rheometer optimum) | 130 | 165 | 160 | 155 | 110 |

*Source:* Hunt, E. J. and Alliger, G., *Radiat. Phys. Chem.*, 14, p. 39. (With permission from
Elsevier Ltd.)

**TABLE 8.7B**

Physical Properties from Vulcanized Bromobutyl Inner Liner Compound
(Aged 240 h at 125°C)

| Property | Nominal Radiation Dose, kGy | | | | |
|---|---|---|---|---|---|
| | 0 | 10 | 20 | 30 | 50 |
| Hardness, durometer A | 60 | 53 | 55 | 54 | 55 |
| 100% modulus, MPa | 2.2 | 1.8 | 1.8 | 1.8 | 1.9 |
| 300% modulus, MPa | 6.9 | 6.4 | 6.4 | 6.3 | 6.4 |
| Tensile strength, MPa | 8.4 | 7.5 | 7.5 | 7.2 | 7.3 |
| Elongation at break, % | 420 | 390 | 400 | 390 | 380 |
| Fatigue, kGy (cured to rheometer optimum) | 25 | 60 | 50 | 45 | 40 |

*Source:* Hunt, E. J. and Alliger, G., *Radiat. Phys. Chem.*, 14, p. 39, 1979. (With permission from Elsevier Ltd.)

level, and consequently, the factory floor provides the bulk of the shielding. Further improvements were in designing the shielding structure from a combination of lead and steel, replacing the traditional concrete vault.

The components that are supported by cords or fabric can be treated on-line easily by using a system of pulleys. This, unfortunately, is not yet possible for unsupported components, such as inner liner and other low-tension materials.[58,59]

The current technology is very cost-effective. If applied correctly in line with other processes, such as extrusion or calendering, it can produce substantial savings by the reduction in material or the tire component's weight. The reduction of overall thickness can be as much as 20%.[59]

## 8.3 Electron Beam Process in the Manufacture of Polyolefin Foams

The thin, highly stretched expanding foam cells of thermoplastic melts are unstable and bound to rupture at elevated temperatures when not stabilized. This is particularly important when chemical blowing agents are used, since they require relatively high temperatures to decompose. One of the methods of stabilization of polyolefin melt is cross-linking. Cross-linking not only stabilizes bubbles during expansion, but also enhances the cellular product from thermal collapse, which is necessary in some applications.

Electron beam irradiation is one of the methods of cross-linking in this process.[60] The other methods use peroxide,[61,62] multifunctional azide,[63–66] or an organofunctional silane.[67] Polyethylene resins respond to electron beam irradiation well since the rate of cross-linking exceeds significantly the chain scission. Polypropylene (PP) is prone to β-cleavage, which makes it difficult to cross-link by a free radical process.[67] For that reason, PP resins

require cross-link promoters, such as vinyl monomers, divinyl benzene,[68,69] acrylates and methacrylates of polyols,[70,71] polybutadiene, and others. These compounds promote cross-linking of a polyolefin polymer through inhibiting the decomposition of polymer radicals,[72] grafting,[73] and addition of polymerization-type reactions.[67]

Optimum cross-linking is the most critical requirement for optimum foam expansion. The *gel level* or *gel fraction* is defined as the fraction not soluble in boiling xylene.[74] Excessive cross-linking restricts foam expansion, while insufficient cross-linking results in bubble rupture.[75] The window of optimum cross-linking is fairly narrow; the gel level at the inception of gel expansion needs to be about 20–40%, preferably 30–40%.[76,77] An LDPE resin with a lower value of melt index (higher molecular weight) and a lower density becomes more efficiently cross-linked. A lower-density LDPE has more chain branching, and therefore more tertiary hydrogens, which provide cross-linking sites. Other factors influencing cross-linking are molecular weight distribution and long-chain branching.[76–78] For typical polyethylene, a dosage ranging from 10 to 50 kGy is sufficient to attain the final gel level of 30–40%.

The selection of EB equipment depends on the foam thickness and production rate. The foam manufacturers throughout the world are using equipment with electron accelerators with voltages ranging from 0.5 to 4 MV and power ratings from 10 to 50 kW. The penetration depth of a 1 MV unit is approximately 3 mm (0.12 in.). Irradiation on both sides doubles the thickness capability.[79]

## 8.3.1  Foam Expansion and Its Control

The cross-linked sheet is expanded by means of a chemical blowing agent such as azodicarbonamide, which decomposes in the temperature range between 200 and 210°C (392 to 410°F). In the radiation cross-linking process,[80,81] the cross-linking reaction is completed before the decomposition of the blowing agent and foam expansion. Since the decomposition of the blowing agent and foam expansion occur simultaneously, this process can run twice as fast as peroxide cure, since the heating rate is not restricted by the cross-linking rate.[76] The cell size is easier to control in the cross-linked sheet since the cross-links provide the restricting force against cell growth. Thus, radiation cross-linking favors cell nucleation, and fine uniform cells (typically 0.2–0.3 mm in size) are easily achieved.[82]

## 8.3.2   Manufacturing Processes

A cross-linked polyolefin foam sheet is produced by two methods using chemical cross-linking and by two methods of radiation cross-linking. The two well-established manufacturing processes for polyolefin foams using radiation cross-linking are the *Sekisui* process and *Toray* process. The differences between these two manufacturing methods are mainly in the expansion step, which is almost always done separately. However, the
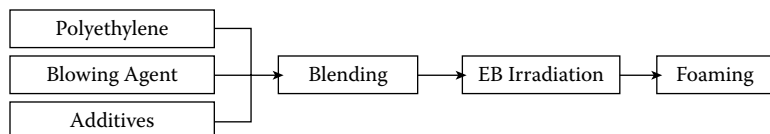
**FIGURE 8.5**
Flow diagram of the manufacturing process for polyolefin foams using radiation cross-linking.

production of the foamable sheet and the cross-linking step are similar. The first step is a uniform mixing of the blowing agent into the polymer melt, followed by sheet extrusion in an extrusion line. Then the cross-linking to the desired degree follows. The flow diagram for this process is in Figure 8.5.

The Sekisui process employs a vertical hot air oven. The foamable sheet is first preheated in the preheating chamber by infrared heaters to about 150°C (302°F) while being supported by an endless belt. The preheated sheet is then expanded in the foaming chamber to temperatures exceeding 200°C (392°F). The expanding sheet supports itself by gravity in the vertical direction. A special tentering device is used to prevent the development of wrinkles in the transverse direction.[83] The advantages of the Sekisui process are the capability of manufacturing a thin sheet and the low energy consumption inherent in the vertical oven.[84] A schematic of the Sekisui foaming oven is in Figure 8.6.
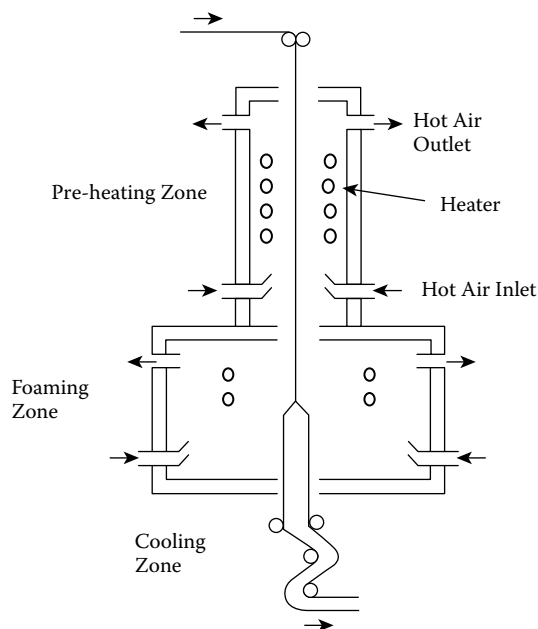


**FIGURE 8.6**
Sekisui foaming oven for polyolefin foams.

**TABLE 8.8**

Comparison of Radiation and Chemical Cross-Linking Processes for Producing Polyolefin Foams

| Item | Radiation Cross-Linking | Chemical Cross-Linking |
| --- | --- | --- |
| Process control | Easy | Difficult |
| Production rate | High | Slow |
| Equipment | Cumbersome | Simple |
| Cost | Decreases with production volume | Relatively constant |
| Blowing agent selection | Easier | More difficult |
| Product thickness, mm | 3–6 | 5–16 |
| Typical cell size, mm | 0.2–0.4 | 0.5–0.8 |
| Cross-link level, % | 30–40 | 60–70 |

In the Toray process, the foamable sheet is expanded as it floats on the surface of molten salts and is heated from the top by infrared lamps. The molten salt mixture consists of potassium nitrate, sodium nitrate, and sodium nitrite.[85] The salt residues from the surface of the foam are blown off by hot air and stripped in water. The Toray process is suitable to produce cross-linked PP foam sheet as well as polyethylene foam sheet. In fact, Toray was the first one to produce commercial PP foam.[86]

### 8.3.3 Comparison of Chemical and Radiation Processes

Both processes have advantages and disadvantages. Currently, they have about an equal share of the global market. The initial investment cost in the irradiation equipment is high, but it is considerably more productive than chemical cross-linking, having the additional advantage of uniform product quality and flexibility of feedstock selection. The product from radiation cross-linked polyolefins is thin, with fine cells and smooth white surfaces. The comparison of chemical and radiation processes is in Table 8.8.[87,88]

## 8.4 Electron Beam Process in the Production of Heat-Shrinkable Materials

Polyolefins, especially polyethylene, can be cross-linked into a material that is elastic when heated. The structure of polyolefins, normally entangled long chains, includes crystalline and amorphous regions. Upon heating above the crystalline melting point of the polymer the crystalline regions disappear.

When cross-linking the polymer, a three-dimensional network is formed. After heating the cross-linked material above its crystalline melting point, the elastic network can be stretched. If the material is cooled in the stretched state below its crystalline melting point, the crystalline regions reform and the material retains its deformation. If it is heated again above the melting temperature, it will shrink back to its original state. This phenomenon is referred to as memory effect and is used for heat-shrink tubing and in packaging.

### 8.4.1 Heat-Shrinkable Tubing

Heat-shrinkable tubing is made typically from polyolefins, PVC, polyvinyl fluoride, PTFE, their blends, or blends with other plastics and elastomers. The formulations may be designed for chemical resistance, heat resistance, flame resistance, etc.[89]

There are essentially two methods to produce shrink tubing from an extruded tube. One of them involves expanding the tube, which had been cross-linked by radiation, heated to temperatures above its crystalline melting point into a sizing tool. The diameter of the sizing tool determines the amount of stretch. The stretched tubing is then cooled down to temperatures below the crystalline melting point in the sizing tool, thus "freezing in" the strain. This method is described in the original Raychem patent (see Figure 8.7). The patent specifies the irradiation dose to be at least about $2 \times 10^6$ rad (20 kGy).[90] Current practice is to irradiate polyethylene tubing with electrons at 1.0 to 2.0 MeV and at a dose of 200–300 kGy. Excessive doses should not be applied; otherwise, the material will have a poorer aging resistance.[91]

The second method is designed to expand the tubing heated above its crystalline melting point into a stationary forming tube or mold by air pressure. The tubing is surrounded by a moving tape over the entire length of the forming device. The tape is formed from a material that does not adhere to the cooled plastic, so it can be readily stripped from the expanded tubing as it emerges from the forming device. The arrangement of the patented process[92] is in Figure 8.8.

Figure 8.9 depicts the process of producing heat-shrinkable polyethylene tubing and the use of the tubing to cover a wire joint. In step I, the tubing is extruded and irradiated to obtain a gel fraction of 40%. In step II, the irradiated tubing is heated up to 140°C (285°F) and expanded by the use of vacuum or pressure to about twice its original diameter, holding its length constant. Steps III and IV show the use of heat-shrinkable tubing to cover a joint of two wires. The tubing is centered over the joint and heated by a hot air gun to a temperature above the crystalline melting point of polyethylene. The sleeve shrinks and becomes a form-fitting cover for the joint.[93]

April 23, 1963                  P. M. COOK ET At                3,086,242
PROCESS AND APPARATUS FOR PRODUCING MATERIALS
HAVING PLASTIC MEMORY
Filed July 15, 1960

FIG. 1.

FIG. 2.

FIG. 3.

PAUL M. COOK
RICHARD W. MUCHMORE
INVENTORS

BY

ATTORNEYS
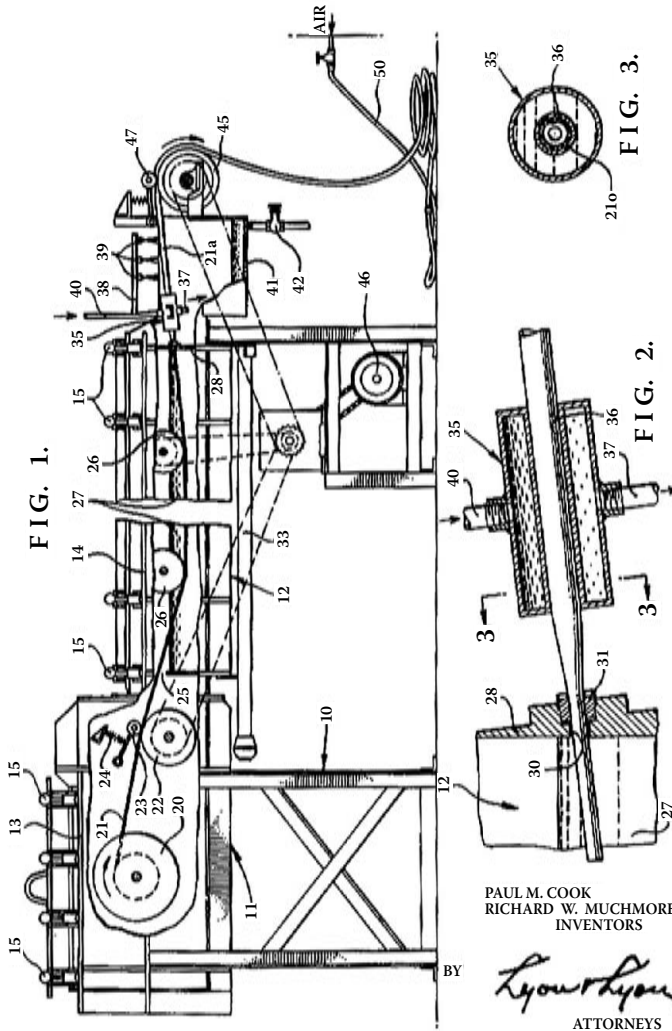
**FIGURE 8.7**
Original Raychem patent for heat-shrinkable tubing.

Thin-walled (approximately 0.010–0.040 in., or 0.25–1.0 mm) tubing is usually selected by continuous service temperature, which may range from 90°C (194°F) for some PVC tubing up to 250°C (482°F) for tubing made from PTFE. The main use of thin shrink tubing is in electrical and electronic applications.

FIG. 4.

FIG. 1.

AIR PRESSURE
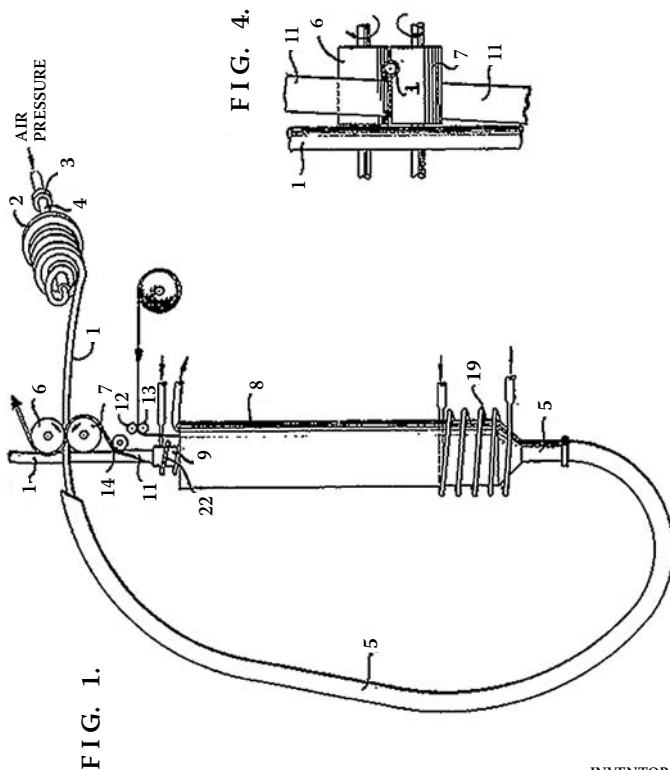
**FIGURE 8.8**
Alternative patented method of producing heat-shrinkable tubing.

Tubing with thicker walls (typically in the range of 0.080 to 0.170 in., or 2 to 4 mm) is fabricated mainly from polyolefins and is used to cover splices in the telecom, CATV, and electric power industries. Often such tubing is combined with mastic or hot melt that aids in forming an environmental barrier for the splice. Diameters of the heavy wall tubing may be up to 7 in. (178 mm)
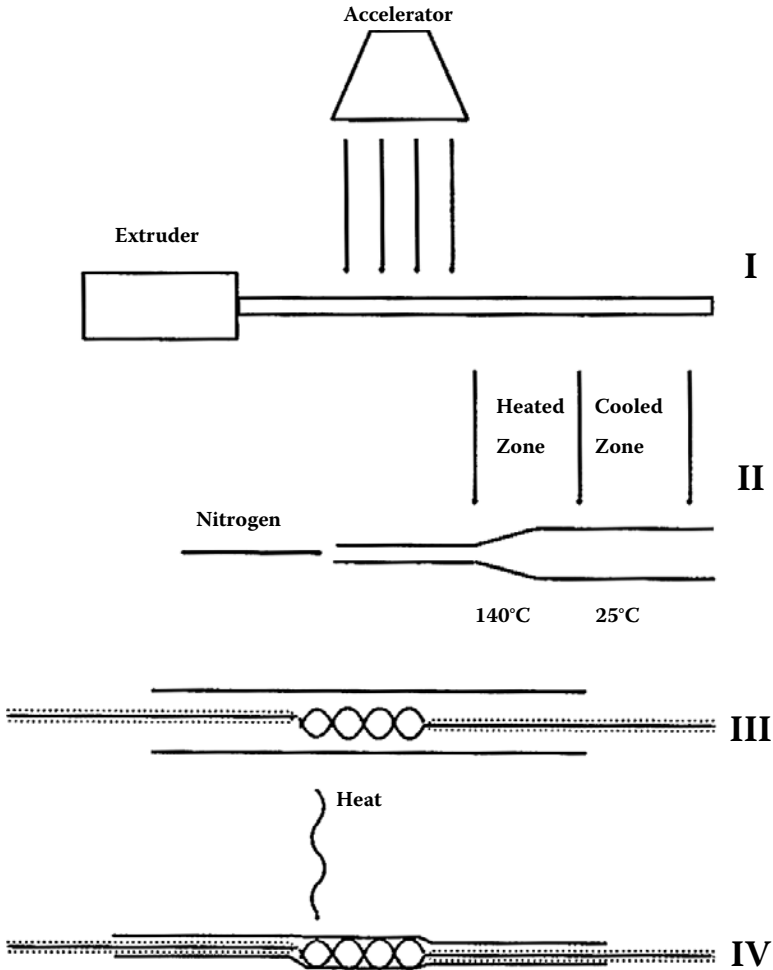
**FIGURE 8.9**
Production and application of heat-shrinkable tubing on a wire splice. (*Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.) Carl Hanser Publishers, p. 20 (1992). With permission from Carl Hanser Publishers.)

or even 12–24 in. (300 to 600 mm) when used as corrosion protection sleeves on weld joints of gas and oil pipelines.[94]

## 8.4.2 Heat-Shrinkable Sheets and Films

Heat-shrinkable sheets (thickness 0.040 to 0.120 in., or 1–3 mm) and films (thickness 0.001 to 0.020 in., or 0.025 to 0.5 mm) are fabricated from many of the same materials as shrinkable tubing.[93] They are produced by extrusion as a tube, sheet, or blown film. Irradiation is done by the equipment shown
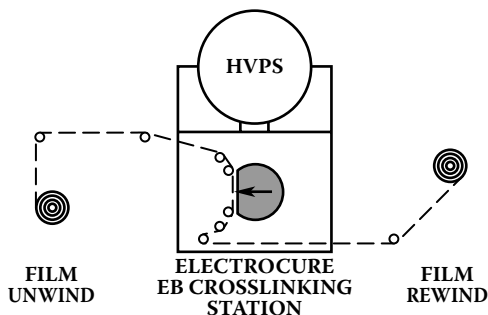
**FIGURE 8.10**
Electron beam processor for film conversion. HVPS, high-voltage power supply. The arrow in the
EB curing unit indicates the direction of the electron beam. (Courtesy Energy Sciences, Inc.)

in Figure 8.10. Orientation (stretching) after irradiation can be performed by
several methods, namely, by differentially heated and driven rolls (in the
machine direction) or by a tenter frame (across the machine direction), as
shown in Figure 8.11.

Heat shrink sheets are used for many of the same applications as heavy
wall shrink tubing. The advantage of the sheet over a tube is that it can be
conveniently slipped over the area to be protected, for example, over continu-
ously installed cable. There are many methods to close the heat-shrinkable
sheets, such as zippers, rail and channel, heat-sealable bonds, etc., some of
them patented.[95–98]

Heat-shrinkable films have found wide use in food wrap and packaging.
The original development was done in the late 1950s by W. R. Grace and Co.,
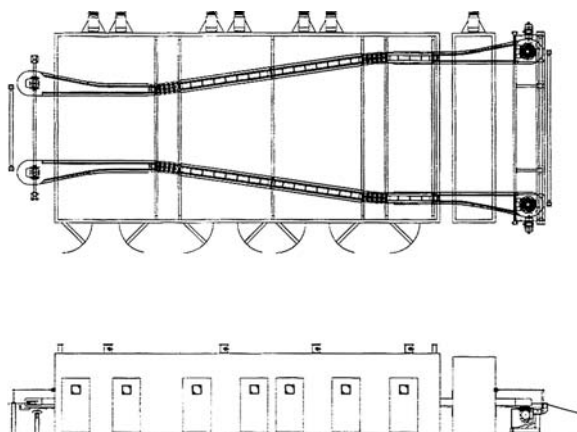


**FIGURE 8.11**
Tenter frame for transverse direction orientation of sheets and films. (Courtesy of Marshall &
Williams Plastics.)

and the process is still used for much more sophisticated multilayer lami-
nated films with superior barrier properties,[98–101] exceptionally high tear
strength,[102] or for multilayer films with low shrink force for packaging of
easily deformable articles.[103] The currently used doses for PE films are 200–
300 kGy at electron energy in the range of 0.5–1.0 MeV.[90]

## 8.5  Electron Beam Process in Coatings, Adhesives, Paints, and Printing Inks

These applications are a domain that UV and EB processes share since both
can directly convert reactive liquids into solids almost instantly. There are
specific areas where EB irradiation is more suitable than the UV curing pro-
cess. In general, these include applications where thick layers of coatings
or adhesives are applied. Other instances are coatings with high levels of
inorganic pigments or fillers, which usually cannot be cured by UV radiation
because of their opacity. As pointed out earlier, the capital cost of standard
EB curing equipment is considerably higher than that of a UV curing line.
However, a recent trend is to build smaller electron beam processors operat-
ing at a much lower voltage (see Section 3.2.3). Such machines are consider-
ably less expensive and consequently represent formidable competition to
UV curing equipment in an increasing number of applications. At any rate,
EB curing lines operate at much higher line speeds and compare favorably
if they are used for continuous long runs. In this section, discussion will be
limited to applications specific to the EB curing process or possibly a combi-
nation of EB and UV.

### 8.5.1  Magnetic Media

Magnetic media, such as magnetic tapes for audio and video recording,
program cards of various types, and computer diskettes, have an important
place in the electronic industry. The magnetic particles, such as gamma fer-
ric oxide, ferric oxide with $Cr^{+2}$, chromium oxide, and iron-cobalt alloys, are
dispersed in a solution of a binder.[104] The binders include polyurethanes,
vinylchloride/vinyl acetate copolymers, vinylchloride/vinyl acetate/vinyl
alcohol copolymers, polyacrylates, nitrocellulose, and others. Particularly
important are blends of polyurethanes with other polymers.[105] The sub-
strates used for tapes and other forms of magnetic media are polyvinyl-
chloride, poly(ethylene terephtalate), and other film-forming polymers, with
poly(ethylene terephtalate) being currently most widely used.[106]

   The electron beam is very well suited for the production of most of the
magnetic media, such as high-density floppy disks and magnetic tapes. In

this process, the substrate is coated with a coating containing a large volume of magnetic particles. The uncured coating passes first through a magnetic field to orient the particles, and then through the EB processor. The high loading of the magnetic particles excludes the use of UV cure. The electron beam offers several advantages: The high reaction rate virtually eliminates surface contamination closely associated with thermal cure. The high degree of cross-linking of the binders used in the coatings gives a tougher and more wear-resistant surface.

### 8.5.2  Coatings

Most of the EB units sold in the recent past were mainly for release coating applications. New chemistry has been commercialized, but further developments are needed to satisfy this market segment.[107]

Another process where electron beam equipment is widely used is curing of overprint varnishes (OPVs). OPV is applied over a printed surface to protect the ink layer and to improve the appearance of the product.[107] The exceptionally high gloss of such finishing coatings and varnishes is achieved specifically by EB cure.[108,109]

Typical applications of EB curing in protective and decorative coatings include:[110]

- Wood finishes (doors, front panels of furniture, lamination and lacquer finishes)
- Paper coatings and finishes (paper laminates for wood decoration, high-gloss paper for gift wrapping, lacquer on metallized paper)
- Film coatings (antistatic coatings, antiscratch coating on phone and other cards)

Coatings on *rigid substrates*, mainly on wood (doors, furniture, laminated panels), often have a fairly thick coating (up to 200 $g/cm^2$), and consequently require electrons with relatively high energy. However, production rates are mostly dependent on other operations, such as feeding, discharge, and polishing, and therefore, low to moderate beam powers are sufficient.

Coatings on *flexible substrates* are considerably thinner, typically in the range of 130 $g/cm^2$, but the production rates are high (100 to 300 m/min); therefore, lower energy electrons and moderate to high power beams are required.[110]

In some cases, a hybrid system (a combination of UV and EB cures) is used to ensure a sufficient degree of cross-linking through the coating or a sufficient adhesion to the substrate. An additional benefit of such a hybrid system is the control of gloss and surface finish.[111]

An example of EB curing of coatings is shown in Figure 8.12, and that of a curing line for a hybrid UV/EB process in Figure 8.13.
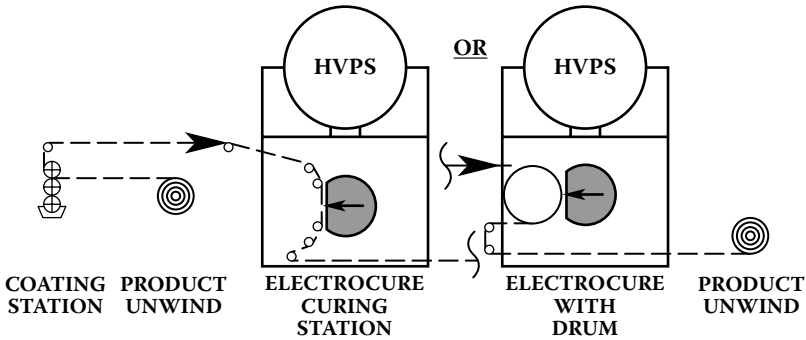
**FIGURE 8.12**
Electron beam processor for curing coatings. HVPS, high-voltage power supply. The arrow in the EB curing unit indicates the direction of the electron beam. (Courtesy Energy Sciences, Inc.)

### 8.5.3 Printing and Graphic Arts

With the advent of less expensive and more compact electron beam processors, a growing number of printers/converters in graphic arts are exploring the possibility to use this process as an alternative to conventional ink/coating drying.[112]

Currently, the following EB cure applications in printing and graphic arts are reported in the literature:[109,113]

- High-gloss cosmetic and cigarette packaging
- Greeting cards
- Aseptic packaging
- Record album jackets
- Stamps
- Banknotes
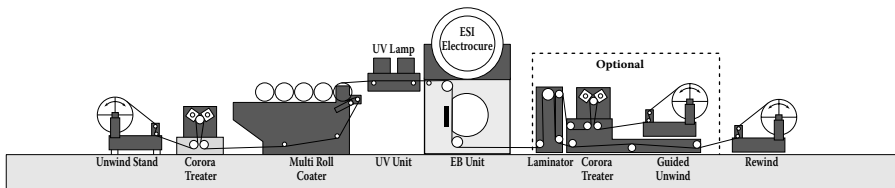


A. Unwind – Coating Station – UV Curing – EB Curing – Rewind.
   *OR:*
B. Unwind – Coating Station – UV Curing – EB Curing – **Optional
   Second Web Unwind and Lamination Station** – Rewind.

**FIGURE 8.13**
Coating line for a hybrid UV/EB curing process for coatings. (Courtesy Faustel Corporation.)
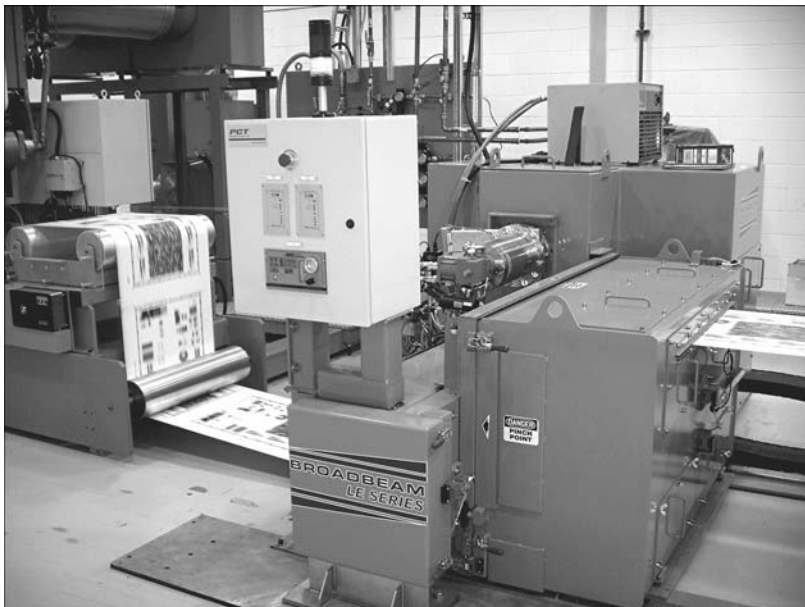
**FIGURE 8.14**
Low-voltage EB equipment on web offset press. (Courtesy of PCT Engineered System, LLC).

The most common installation of EB equipment is at the end of a web offset press used for the production of folding cartons (Figure 8.14). Offset (lithographic) printing uses paste inks, which are designed to be "wet trapped" without any interstation drying. That allows placing a single EB unit at the end of the press.[114] The development of compact low-voltage EB equipment has allowed for their use to cure inks on flexible packaging, polyester, and polypropylene films and labels.[115,116] The low-voltage permanent vacuum modular equipment has potential to be used for EB curing between the stations.[114]

### 8.5.4 Adhesives

In the field of adhesives, electron beam curing has been used mainly in pressure-sensitive and laminating adhesives.[117]

#### 8.5.4.1 Pressure-Sensitive Adhesives (PSAs)

The main property that distinguishes a pressure-sensitive adhesive from other types of adhesives is that it exhibits a permanent and controlled tack. This tackiness is what causes the adhesive to adhere instantly when it is pressed against a substrate. After it adheres, the PSA should exhibit tack, peel, and shear properties, which are reproducible within

narrow limits. This requires that the adhesive layer be only slightly cross-linked.[118] PSAs are based on polymers with low $T_g$, typically in the range of –74 to +13°C.[119]

Because of the precise control of the degree of cross-linking attainable by the electron beam process, it is well suited for the production of PSAs. Recent developments in EB design, particularly lower voltage, and materials developments have made electron beam curing of pressure-sensitive adhesives affordable, practical, and possible.[120–122]

### 8.5.4.2  Laminating Adhesives

Laminating adhesives are used to bond layers of different materials together. There are many possible combinations, including different polymers, copolymers, papers, foils, fabrics, films, metals, glass, etc. The bond between the individual layers has to be sufficiently strong to hold the laminate together. This is accomplished by applying the adhesive in the molten state (hot melt) and creating the bond upon cooling or by cross-linking. Cross-linking can be accomplished by using a reactive adhesive, consisting of two components, which react when mixed (e.g., polyurethanes or epoxies), or by radiation.

Cross-linking increases the cohesive strength of the adhesive and consequently the bond strength. Many of the materials used for laminations are transparent to light, and these can easily be cured by UV or visible light. However, if the laminated materials are opaque to UV and visible light, it may be cross-linked by electron beam since high-energy electrons penetrate paper, foils, and fabrics.

Electron beam curing has been used for curing laminating adhesives in flexible packaging, and this application has been growing rapidly after the introduction of low-voltage compact EB processors. The advantages of EB curing of laminating adhesives are:[123,124]

- Adhesives do not use solvents
- Adhesive is one part chemistry (no mixing needed)
- Long shelf-life (more than 6 months)
- Adhesive remains unchanged until it is cured
- No multiroll coating needed
- No complex tension controls needed
- Adhesive bond established almost instantly
- Real-time quality control
- In-line processing, immediate shipment possible
- Easy cleanup

Advantages over UV curable laminating adhesives are:[124]

- EB penetrates opaque films.
- EB produces typically higher conversion.
- Most EB systems cure without photoinitiators (simpler formulation, cost saving, fewer residues and extractables).

Recently a solvent-free dual-cure laminating adhesive based on the combination of polyurethane chemistry and EB cure was developed that exhibits improved properties compared to laminates prepared by either method alone.[125]

### 8.5.5 Polymeric Fiber-Reinforced Composites

Fiber-reinforced composites are materials combining high strength with a low weight. Polymeric composite materials consist of a thermoset or thermoplastic matrix and reinforcing fibers. The main functions of the matrix are to act as a binder for the fibers, to transfer forces from one fiber to the other, and to protect them from environmental effects and effects of handling. The reinforcing fibers can be continuous or discontinuous (short fibers) and may be oriented within the matrix at different angles. Short fibers are frequently dispersed in the matrix randomly, although some composite materials may contain oriented short fibers.

The performance characteristics of a composite material depend on the type of reinforcing fiber (its strength and stiffness), its length, fiber volume fraction in the matrix, and the strength of the fiber-matrix interface. The presence of voids and the nature of the matrix are additional but minor factors.

The majority of commercially available polymeric composites are reinforced by glass fibers, carbon fibers, aramid fibers (e.g., Kevlar) and, to a lesser degree, boron fibers. In some cases hybrid composites are made that contain combinations of fibers.

Matrix materials for commercial composites are mainly liquid thermosetting resins such as polyesters, vinyl esters, epoxy resins, and bismaleimide resins. Thermoplastic composites are made from polyamides, polyether ether ketone (PEEK), polyphenylene sulfide (PPS), polysulfone, polyetherimide (PEI), and polyamide-imide (PAI).

Thermosetting composites are cured at either ambient or elevated temperatures to obtain a hard solid by cross-linking. The use of radiation cross-linking decreases the cure time considerably. In particular, an electron beam has been used successfully in many instances. For example, glass-fiber-reinforced composites cured by electron beam have been used for the production of cladding panels.[126]

The production of materials having good mechanical properties matching those produced by conventional thermal methods has been achieved by

using EB processing, and a growth in these applications is expected.[125,126] Graphite-fiber-reinforced composites with low stress and exhibiting little shrinkage upon cure have been produced with a performance comparable to that of state-of-the-art toughened epoxy resins.[127–129] A layer-by-layer electron beam curing process of filament-wound composite materials using low-energy electron beams has been developed. This process has a wide range of applications in the aerospace technology.[130,131] A variety of different curing methods leading to successful products are described in the literature.[132–135]

The article of Berejka[136] covers the state of the art in electron beam technology, material technology, and product-forming technology as applied to structural carbon-fiber-reinforced polymeric composites.

A great deal of work was done to develop methods for using electron beam technology for the manufacture and repair of advanced composites. Many benefits have been identified for EB curing fiber-reinforced composites, including lower residual stresses that result from curing at ambient or subambient temperatures, shorter curing time for individual components (minutes vs. hours), improved material handling (the resins have unlimited shelf life), and possible process automation in the placement of fiber reinforcement. The only process EB cannot use is resin transfer molding (RTM), since the electron beam cannot penetrate massive molds used to mold the composite parts.[137] So far, mainly EB curable cationic-initiated epoxy resins have been used. Although most of the development work was geared toward aerospace, the technology is applicable to other industries, including automotive, consumer goods etc.

The development work also yielded UV curable adhesives for aluminum to aluminum, graphite to aluminum, and graphite to graphite.

So far several parts have been produced by applying EB technology:

- Lower- and upper-wing assembly
- Liquid hydrogen tank

Another viable application is the use of EB curing in the repair of aircraft composite parts. It was determined that most of the repairs are completed in 50–70% of the time required for a normal thermal repair.[137]

### 8.5.6 Hydrogels

Hydrogels are three-dimensional hydrophilic polymeric structures able to absorb large quantities of water. They are synthesized by polymerization of hydrophilic monomers. The extent of the reversible swelling and deswelling property of these materials is known to depend on the nature of both intermolecular and intramolecular cross-linking, as well as the degree of hydrogen bonding in the polymer network. Increasingly, these hydrogels are being utilized in a variety of applications, including drug release, biosensors, tissue engineering, and pH sensors. To date, a variety of compounds have been

utilized in the synthesis of hydrogels. Examples of monomers employed for this purpose include *N*-isopropylacrylamide (NIPAM), vinyl alcohol, ethylene glycol, and *N*-vinyl pyrrolidone (NVP).[138] These monomers can be combined with natural polymers, such as agar.[139]

Radiation techniques are very suitable tools for the production of hydrogels. An example of a mature technology of this kind is hydrogel wound dressings, now being produced on large scale.[140] Other practical applications are contact lenses (silicone hydrogels, polyacrylamides), dressings for the healing of burn victims and other hard-to-heal wounds, disposable diapers, and similar highly absorbing products.[139]

The most widely used hydrogels are based on polyethylene oxides (PEOs) dissolved at relatively low concentrations in water (typically 4 to 5%). Modest radiation exposure (less than 10 kGy) is needed to form the gel. Gels as thick as 2 mm (80 mils) are being produced.

Emerging applications include a hydrogel-based system for anticancer therapy due to local drug delivery, systems for encapsulation of living cells, a new approach to the synthesis of polymeric material for intervertebral discs implant, temperature-sensitive membranes, hydrogel phantoms of a 3D radiation dosimeter for radiotherapy, degradation-resistant nanogels and microgels for biomedical purposes (e.g., synovial fluid substitute), and hydrogel-based dietary products.[140]

Another application reported[141] is preparing hydrogels from a mixture of polyvinyl alcohol (PVA) and carboxymethyl cellulose (CMC) using freezing and thawing and EB irradiation. The blend having the composition 80/20 (CMC/PVA) was used as a super absorbent in the soil for agriculture. Moreover, the water retention increased in the soil containing this hydrogel. Thus, this type of hydrogel can be used to increase water retention in desert regions.

Other hydrogels are prepared from poly($\alpha$-hydroxylic) acids, e.g., lactic acid, polyacrylic acid, acrylamides and acrylated polyvinyl alcohol,[142] and polyethylene glycol.

## References

1. Mehnert, R., Bögl, K. W., Helle, N., and Schreiber, G. A., in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A22 (Elvers, B., Hawkins, S., Russey, W., and Schulz, G., Eds.), VCH Verlagsgesselschaft, Weinheim, p. 484 (1993).
2. McGinnis, V. D., in *Encyclopedia of Polymer Science and Engineering*, Vol. 4 (Mark, H. F., and Kroschwitz, J. I., Eds.), John Wiley & Sons, New York, p. 445 (1986).
3. Yongxiang, F., and Zueteh, M., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser, Munich, p. 72 (1992).
4. Levy, S., and DuBois, J. H., *Plastic Product Design Handbook*, Van Nostrand Reinhold, New York (1977).
5. Rosen, S., *Fundamental Principles of Polymeric Materials*, John Wiley & Sons, New York (1982).

6. Williams, H., *Polymer Engineering*, Elsevier, New York (1975).
7. Roberts, B. E., and Verne, S., *Plast. Rubber Process Appl.*, 4, p. 135 (1984).
8. Hochstrasse, U., *Wire Industry*, 46, January (1985).
9. Markovic, V., *IAEA Bulletin*, Spring (1985).
10. Brand, E. S., and Berejka, A. J., *World*, 179, p. 49 (1978).
11. Clelland, M. R., *Radiat. Phys. Chem.*, 18, p. 301 (1981).
12. Yongxiang, F., and Zueteh, M., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser, Munich, p. 73 (1992).
13. Barlow, A., Hill, L. A., and Meeks, L. A., *Radiat. Phys. Chem.*, 14, p. 783 (1979).
14. Bly, J. H., *Radiat. Phys. Chem.*, 9, p. 599 (1977).
15. Yongxiang, F., and Zueteh, M., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser, Munich, p. 74 (1992).
16. Bruins, P. F., *Plastics for Electrical Insulation*, Wiley-Interscience, New York (1968).
17. Harrop, P., *Dielectrics*, Butterworth, London (1972).
18. *Testing of Polymers* (Schmitz, J. V., Ed.), Vol. 1, Wiley-Interscience, New York (1965).
19. AEIC 5-79, *Specifications, PE Power Cables* (5–69 kV).
20. ASTM D150, *AC Loss Characteristics and Dielectric Constants*, American Society of Testing Materials, Philadelphia, PA.
21. Blythe, A. R., *Electrical Properties of Polymers*, Cambridge University Press, London (1979).
22. Yongxiang, F., and Zueteh, M., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, p. 76 (1992).
23. Wintle, H. J., in *Radiation Chemistry of Macromolecules* (Dole, M., Ed.), Academic Press, New York (1972).
24. Yongxiang, F., and Zueteh, M., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, p. 77 (1992).
25. Charlesby, A., and Fydelor, P. J., *Radiat. Phys. Chem.*, 4, p. 107 (1972).
26. Schnabel, W., *Polymer Degradation*, Maxmillan, New York (1981).
27. Ueno, K., *Lecture Notes on Formulation of Radiation Cross-Linking Compounds*, IAEE Training Course, Shanghai, September (1989).
28. DuBois, J. H., and John, F. W., *Plastics*, Van Nostrand Reinhold, New York (1974).
29. Matsuoka, S., *IEEE Trans. Nuclear Sci.*, NS-23, p. 1447 (1976).
30. Sasaki, T., et al., *Radiat. Phys. Chem.*, 14, p. 821 (1979).
31. Barlow, A., Briggs, J. W., and Meeks, L. A., *Radiat. Phys. Chem.*, 18, p. 267 (1981).
32. Chapiro, A., *Radiation Chemistry of Polymer Systems*, Wiley-Interscience, New York (1962).
33. Salovey, R., and Gebauer, R., *J. Polym. Sci.*, A-1, p. 1533 (1972).
34. Yongxiang, F., and Zueteh, M., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser, Munich, p. 80 (1992).
35. Waldron, R. H., Mc Rae, H. F., and Madison, J. D., *Radiat. Phys. Chem.*, 25, p. 843 (1988).
36. Peshkov, I. B., *Radiat. Phys. Chem.*, 22, p. 379 (1983).
37. Yongxiang, F., and Zueteh, M., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser, Munich, p. 81 (1992).
38. Becker, R. C., Bly, J. H., Cleland, M. R., and Farrell, J. P., *Radiat. Phys. Chem.*, 14, p. 353 (1979).
39. Cleland, M. R., *Technical Information Series, TIS 77-12*, Radiation Dynamics, Melville, NY (1977).

40. McLaughlin, W. L., et al., *Dosimetry for Radiation Processing*, Taylor and Francis, London (1989).
41. Zagorski, Z. P., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, Chapter 13 (1992).
42. Yongxiang, F., and Zueteh, M., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, p. 82 (1992).
43. Studer, N., and Schmidt, C., *Wire J. Int.*, 17, p. 94 (1984).
44. Cleland, M. R., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, p. 81 (1992).
45. Yongxiang, F., and Zueteh, M., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser, Munich, p. 84 (1992).
46. Yongxiang, F., and Zueteh, M., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, p. 81 (1992).
47. Luniewski, R. S., and Bly, J. H., in *Proceedings of Regional Technical Conference "Irradiation and Other Curing Techniques in the Wire Industry,"* Newton, MA, March 20–21 (1975).
48. Barlow, A., Biggs, J., and Maringer, M., *Radiat. Phys. Chem.*, 9, p. 685 (1977).
49. Clelland, M. R., *Accelerator Requirements for Electron Beam Processing*, Technical Paper TIS 76-6 from Radiation Dynamics, Inc., Melville, NY (1976).
50. Clelland, M. R., *Lecture Notes on Electron Beam Processing, IAEA Regional Training Course*, Shanghai (1988).
51. Timmerman, U.S. Patent 3,142,629 to Radiation Dynamics, Inc. (July 1964).
52. *Vulcanization of Vistalon Polymers*, ExxonMobil Chemical (2000).
53. Tada, S., and Uda, I., *Radiat. Phys. Chem.*, 22, p. 575 (1983).
54. Sawasaki, T., and Nojiri, A., *Radiat. Phys. Chem.*, 31, p. 877 (1988).
55. Yongxiang, F., and Zueteh, M., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Hanser, Munich, p. 88 (1992).
56. Hunt, E. J., and Alliger, G., *Radiat. Phys. Chem.*, 14, p. 39 (1979).
57. Thorburn, B., and Hoshi, Y., Meeting of Rubber Division of American Chemical Society, Detroit, October 8–11, Paper 89 (1991).
58. Thorburn, B., Meeting of Rubber Division of American Chemical Society, Chicago, April 19–22, Paper 20 (1994).
59. Thorburn, B., and Hoshi, Y., Meeting of Rubber Division of American Chemical Society, Anaheim, CA, May 6–9, Paper 89 (1997).
60. Charlesby, A., *Nucleonics*, 12, p. 18 (1954).
61. Ivett, R. N., U.S. Patent 2,826,540 to Hercules Powder Co. (1958).
62. Precopio, E. M., and Gilbert, R., U.S. Patent 2,888,424 (1959).
63. Lewis, J. R., Japanese Patent Publication 40-25 351 to Hercules Powder Co. (1965).
64. Palmer, D. A., U.S. Patent 3,341,481 to Hercules, Inc. (1967).
65. Palmer, D. A., U.S. Patent Re 26 850 to Hercules, Inc. (1970).
66. Scott, H. G., U.S. Patent 3,646,155 to Midland Silicones Ltd. (1972).
67. *Di-Cup® and Vul-Cup® Peroxides Technical Data*, Bulletin PRC-102A, Hercules, Inc., Wilmington, DE (1979).
68. Griffin, J. D., Rubens, L. C., and Boyer, R. F., Japanese Patent Publication 35-13 138 (1960); British Patent 844-231 to Dow Chemical Co. (1960).
69. Okada, A., et al., U.S. Patent 3,542,702 to Toray Industries, Inc. (1970).
70. Atchinson, G., and Sundquist, D.J., U.S. Patent 3,852,177 to Dow Chemical Co. (1974).

71. Nojiri, A., Sawasaki, Y., and Koreda, T., U.S. Patent 4,367,185 to Furukawa Electric Co. Ltd. (1983).
72. Lohmar, E., and Wenneis, W., U.S. Patent 4,442,233 to Firma Carl Freudenberg (1984).
73. Nojiri, A., and Sawasaki, T., *Radiat. Phys. Chem.*, 26, p. 339 (1985).
74. ASTM D2765, Method A, Vol. 08.02, American Society for Testing Materials, Philadelphia, PA.
75. Benning, C. J., *J. Cell. Plast.*, 3, p. 62 (1967).
76. Trageser, D. A., *Radiat. Phys. Chem.*, 9, p. 261 (1977).
77. Harayama, H., and Chiba, N., *Kino Zairo*, 2, p. 30 (1982).
78. Shina, N., Tsuchiya, M., and Nakae, H., *Japanese Plastic Age*, December, p. 37 (1972).
79. Sakamoto, I., and Mizusawa, K., *Radiat. Phys. Chem.*, 22, p. 947 (1983).
80. Shinohara, Y., Takahashi, T., and Yamaguchi, K., U.S. Patent 3,562,367 to Toray Industries, Inc. (1971).
81. Sagane, N., et al., U.S. Patent 3,711,584 to Sekisui Chemical Co. Ltd. (1973).
82. Park, C. P., in *Polymeric Foams* (Klempner, D., and Frisch, K. C., Eds.), Hanser, Munich, Chapter 9, p. 211 (1991).
83. Kiyono, H., et al., U.S. Patent 4,218,924 to Sekisui Chemical Co. (1980).
84. Park, C. P., in *Polymeric Foams* (Klempner, D., and Frisch, K. C., Eds.), Hanser, Munich, Chapter 9, p. 231 (1991).
85. Shinohara, Y., et al., U.S. Patent 3,562,367 to Toray Industries, Inc. (1971).
86. Tamai, I., and Yamaguchi, K., *Japanese Plastic Age*, December 22 (1972).
87. Harayama, H., and Chiba, N., *Kino Zairo*, 2, p. 30 (1982).
88. Park, C. P., in *Polymeric Foams* (Klempner, D., and Frisch, K. C., Eds.), Hanser, Munich, Chapter 9, p. 234 (1991).
89. Bradley, R., *Radiation Technology Handbook*, Marcel Dekker, New York, p. 247 (1983).
90. Cook, P. M., and Muchmore, R. W., U.S. Patent 3,086,242 to Raychem Corporation (1963).
91. Mehnert, R., Bögl, K.W., Helle, N., and Schreiber, G. A., in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A22 (Elvers, B., Hawkins, S., Russey, W., and Schulz, G., Eds.), VCH Verlagsgesselschaft, Weinheim, p. 487 (1993).
92. Timmerman, R., U.S. Patent 3,296,344 to Radiation Dynamics, Inc. (1967).
93. Silverman, J., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, Chapter 2, p. 20 (1992).
94. Bradley, R., *Radiation Technology Handbook*, Marcel Dekker, New York, p. 248 (1983).
95. Ellis, R. H., U.S. Patent 3,455,336 to Raychem Corporation (1969).
96. Derbyshire, R. L., U.S. Patent 4,287,011 to Radiation Dynamics, Inc. (1981).
97. Muchmore, R. W., U.S. Patent 3,542,077 to Raychem Corporation (1970).
98. Dyer, D. P., Tysinger, A. D., and Elliott, J. E., U.S. Patent 6,326,550 to General Dynamics Advanced Technology Systems, Inc. (2001).
99. Brax, H. J., Porinchak, J. F., and Weinberg, A. S., U.S. Patent 3,741,253 to W. R. Grace & Co. (1973).
100. Mueller, W. B., et al., U.S. Patent 4,188,443 to W. R. Grace & Co. (1980).
101. Bornstein, N. D., et al., U.S. Patent 4,064,296 to W. R. Grace & Co. (1977).
102. Kupczyk, A., and Heinze, V., U.S. Patent 5,250,332 to RXS Schrumpftechnik Garnituren G.m.b.H, Germany (1993).
103. Bax, S., Ciocca, P., and Mumpower, E. L., U.S. Patent 6,150,011 to Cryovac, Inc. (2000).

104. Koleske, J. V., *Radiation Curing of Coatings*, ASTM International, West Conshohocken, PA, p. 213 (2002).
105. Santorusso, T. M., *Radiation Curing*, 11, No. 3, August, p. 4 (1983); *Proceedings, Radcure '84*, Atlanta, GA, September 10–13, p. 16 (1984).
106. Zillioux, R. M., *Proceedings of Radcure '86*, Baltimore, MD, September 8–11, p. 8 (1986).
107. Mehnert, R., Pinkus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV&EB Curing Technology and Equipment*, Vol. 1, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 34 (1978).
108. Maguire, E. F., *RadTech Report*, 12, No. 5, September/October, p. 18 (1998).
109. Seidel, J. R., in *Radiation Curing of Polymers* (Randell, D. R., Ed.), The Royal Society of Chemistry, London, p. 12 (1987).
110. Mehnert, R., Bögl, K. W., Helle, N., and Schreiber, G. A., in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A22 (Elvers, B., Hawkins, S., Russey, W., and Schulz, G., Eds.), VCH Verlagsgesselschaft, Weinheim, p. 485 (1993).
111. Hara, K. J., in *Radiation Curing of Polymers* (Randell, D. R., Ed.), The Royal Society of Chemistry, London, p. 127 (1987).
112. Biro, D. A., *RadTech Report*, 16, No. 2, March/April, p. 22 (2002).
113. Gamble, A. A., in *Radiation Curing of Polymers* (Randell, D. R., Ed.), The Royal Society of Chemistry, London, p. 76 (1987).
114. Lapin, S. C., *RadTech Report*, 22, No. 5, September/October, p. 27 (2008).
115. Meij, R., *RadTech Europe 2005, Conference Proceedings*, Barcelona, October (2005).
116. Sanders, R., *RadTech Report*, 17, No. 5, September/October, p. 30 (2003).
117. Chrusciel, J., *Proceedings RadTech Europe 2001*, Basel, Switzerland, October 8–10, p. 373 (2001).
118. Fisher, R., *Conference Proceedings, TAPPI Hot Melt Symposium 1999*, Durango, CO, June 13–16, p. 115 (1999).
119. Miller, H. C., *J. Adhesive Sealant Council*, p. 111 (1998).
120. Ramharack, R., et al., *Proceedings RadTech North America '96*, April 28–May 2, p. 493 (1996).
121. Nitzl, K., *European Adhesives & Sealants*, 13, No. 4, December, p. 7 (1996).
122. Ramharack, R., et al., *Adhesives Age*, 39, No. 13, December, p. 40 (1996).
123. Rangwalla, I., and Maguire, E. F., *RadTech Report*, 14, No. 3, May/June, p. 27 (2000).
124. Lapin, S. C., *RadTech Report*, 15, No. 4, July/August, p. 32 (2001).
125. Henke, G., *Proceedings RadTech Europe 2001*, Basel, Switzerland, October 8–10, p. 361 (2001).
126. Chaix, C., *RadTech Report*, 11, No. 1, January/February, p. 12 (1997).
127. Walton, T. C., and Crivello, J. V., *Conference Proceedings, '95 International Conference on Composite Materials and Energy*, Montreal, Canada, May 8–10, p. 395 (1995).
128. Singh, A., et al., *Conference Proceedings, '95 International Conference on Composite Materials and Energy*, Montreal, Canada, May 8–10, p. 389 (1995).
129. Walton, T. C., and Crivello, J. V., *Materials Challenge—Diversification and the Future*, Vol. 40, Book 2, Anaheim, CA, May 8–11, p. 1266 (1995).
130. Guasti, F., Matticari, G., and Rossi, E., *SAMPE J.*, 34, p. 29 (1998).
131. Guasti, F., and Rossi, E., *Composites A Appl. Sci. Manuf.*, 28A, No. 11, p. 965 (1997).
132. Raghavan, J., and Baillie, M. R., *Conference Proceedings, Polymer Composites '99*, Quebec, Canada, October 6–8, p. 351 (1999).

133. Crivello, J. V., Walton, T. C., and Malik, R., *Chemistry of Materials*, 9, No. 5, May, p. 1273 (1997).
134. Hill, S., *Materials World*, 7, July, p. 398 (1999).
135. Beziers, D., et al., U.S. Patent 5,585,417 to Aerospatiale Societe Nationale Industrielle (1996).
136. Berejka, A. J., *RadTech Report*, 16, No. 2, March/April, p. 33 (2002).
137. Lopata, V. J., and Sidwell, D. R., *RadTech Repair*, 17, No. 5, September/October, p. 32 (2003).
138. Bhattacharyya, D., Pillai, K., Oliver, M. R., Chyan, T. L., and Timmons, R. B., *Chem Mater.*, 19, p. 2222 (2007).
139. L'Anunziata, M. F., *Radioactivity: Introduction and History*, Elsevier, Amsterdam (2007).
140. Rosiak, J. M., Janik, I., Kadlubowski, S., Kozicki, M., Kujawa, P., Stasica, P., and Ulanski, P., *Nucl. Instrum. Meth. Phys. Res. B*, 208, p. 325 (2003).
141. El Salmawi, K. M., *J. Macromol. Sci. A*, 44, June, p. 619 (2007).
142. Davidson, R. S., *Radiation Curing*, Report 136, 12, No. 4, November, Rapra Technology Ltd., p. 27 (2001).

# 9

## *Dosimetry and Radiometry*

The measurement of the amount of radiant energy delivered by the source is important in order to determine if the equipment operates properly and to ensure that the product will be of required quality. Because of the fundamental difference between UV and EB sources, the measuring methods and instruments are in general different.

## 9.1 EB Dosimetry

Industrial applications of ionizing radiation encompass a wide range of absorbed doses (about six orders of magnitude), dose rates (about twelve orders of magnitude), and energies (over two orders of magnitude).[1]

The absorbed dose is the quantity of interest to be measured in order to evaluate the effects of the radiation on the processed materials. The methods used for that are known as *dosimetry*. There are a multitude of established dosimetric methods, and some of them are listed in Table 9.1.

The main functions of dosimetry are:[1]

- The dose measurement leading to successful processing with a sufficient uniformity
- Process validation, including dose settings for meeting process specifications
- Process qualification, including the establishment and locations and values of minimum and maximum doses
- Process verification, by the coordination of routine dosimetry and the monitoring of process parameters
- Proper calibration and traceability to standards using reference dosimetry

The choice of the method depends on the type of process. With electron beams the critical process parameters are beam energy, beam current, scanning factors and uniformity, beam pulse characteristics, and the configuration of the product being processed.

**TABLE 9.1**

Examples of Dosimetry Systems

| Dosimeter Type | Type of Readout | Examples | Absorbed Dose Range, Gy |
|---|---|---|---|
| Calorimeters | Temperature measurements | Graphite, water, polystyrene | $10^1$–$10^4$ |
| Radiochromic films | Spectrophotometers | Dyed and clear plastic films | $10^0$–$10^6$ |
| Inorganic crystals | EPR[a] spectra | LiF, $SiO_2$ | $10^3$–$10^7$ |
| Organic crystals | EPR[a] spectra | Alanine, sucrose, cellulose | $10^0$–$10^5$ |
| Chemical solutions | Spectrophotometers | Ceric-cerous, organic acids | $10^2$–$10^5$ |
| Semiconductors | Electric measurements | Si diodes | $10^0$–$10^4$ |

[a] EPR = electron paramagnetic resonance.
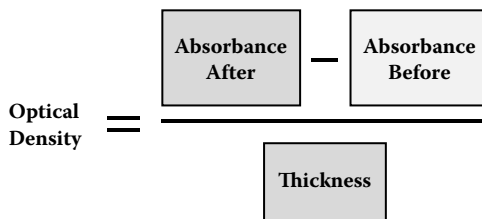
**FIGURE 9.1**
Equation for the change in optical density of film dosimeters.

The most convenient and widely used method is *film dosimetry*, which has been used for several decades. Commercially available film dosimeters are essentially thin plastic films either clear or containing dyes or dye precursors. These so-called *radiochromic films* are available in thicknesses ranging from 0.005 to 1 mm and are used to monitor electron beams and gamma ray doses from 10 to $10^5$ Gy.[2] These doses are typical for medical applications; radiation curing of coatings, adhesives, wire, and cable insulations; cross-linking of shrinkable tubing and films and composites; etc. When irradiated, radiochromic films change irreversibly their optical absorbance in proportion to the absorbed dose (see also Section 9.2.3). To minimize errors due to variation in the film thickness, the dosimeter response is usually expressed as the radiation-induced change in absorbance divided by the dosimeter film thickness (see Figure 9.1). A partial list of currently available EB dosimeters is in Table 9.2. The appropriate test procedures are described in several ASTM standards.[3]

There are several dosimeter systems being used for determining the absorbed dose. The simplest ones are *thin-film dosimeters*, which are suitable for use in routine practice.

**TABLE 9.2**

Examples of Available Thin-Film EB Dosimeters

| Type | Film Thickness, μm | Analysis Wavelength, nm | Dose Range, kGy |
|---|---|---|---|
| Radiachromic films with special dyes: | | | |
| In polyamide (nylon) | 50 or 10 | 600–510 | 0.5–200 |
| In polychlorostyrene | 50 | 630 or 430 | 1–300 |
| In polyvinyl butyral | 22 | 533 | 1–200 |
| Radiachromic microcrystalline layer on a 100 μm polyester support | 6 (sensor) | 650 or 400 | 0.1–50 |
| Cellulose triacetate | 38 or 125 | 280 | 5–300 |
| Dyed cellulose diacetate | 130 | 390 to 450 | 10–500 |
| Dyed (blue) cellophane | 20–30 | 650 | 5–300 |

In general, readings of any dosimeter can be influenced by the following factors:[4]

- Dose rate or dose fractionation
- Temperature, relative humidity, oxygen content, light
- Its stability after irradiation

Each type of dosimeter requires a specific procedure to ensure accurate and reproducible results, such as postirradiation heat treatment. Others need to be stabilized for a certain time (up to 24 h with some) before readings of absorbance are taken.[5–7] The absorbance reading can be done by conventional spectrophotometry or other, more involved methods.

The original radiochromic films were blue cellophane films colored by a blue diazo dye that could be bleached by ionizing radiation, with thicknesses between 19 and 26 μm, depending on manufacturer. Such thin transparent cellophane films have been used as decorative heat-sealable and moisture-resistant packaging films. This might have been one of the reasons why this blue film was found not to be sufficiently reproducible in response to the radiation.[8] Improved cellophane films are produced specifically for dosimetry in two different intense colors, orange and violet, with dissolved disazo dyes. They are delivered in thickness of 1 mil (25.6 μm) and maximum absorptions of 440 and 560 nm, respectively. Bleaching occurs gradually over the dose range 10–300 kGy.[2]

Other commercially radiochromic films are poly(methyl methacrylate) (PMMA), cellulose triacetate (CTA),[1,8] polyamide (nylon) films, poly(vinyl butyrate) with pararosaniline and *p*-nitrobenzoic acid,[1] and alanine films.[2] The CTA films are undyed; PMMA films are available undyed and dyed (red and amber).[2]

Thin-film dosimeters are commonly used for the following measurements:[4]

- The *surface area rate* (or *processing coefficient*), relating the area irradiated per unit time to the beam current, and the absorbed dose is determined by measuring the surface dose at several beam current levels.

- The *cure yield*, calculated in terms of the average absorbed dose delivered to the layer of interest multiplied by the conveyor speed per unit effective beam current. It can be estimated by measuring the dose over the range of beam currents at different speeds.

- The *dose uniformity across the width of the beam*, measured by placing the film chips at about 1 in. (25 mm) intervals or using a long strip of film across the entire width of the beam.

- The *depth dose distribution* is measured by irradiating a stack of radiachromic film chips with a thickness slightly greater than the practical range at the energy of interest. The depth dose is determined by evaluating the individual chips.

**FIGURE 9.2**
Dose reader for irradiated films. (Courtesy of Elektron Crosslinking AB.)

A dose reader designed for direct reading from exposed films, offered by Elektron Crosslinking AB of Sweden, is in Figure 9.2.

To ensure accuracy and reliable data, certain precautions must be taken when using radiochromic films:[2]

- They should not be irradiated in extremes of relative humidity, i.e., below 20% and above 80%. If such conditions cannot be avoided during irradiation, then the films should be sealed in polyethylene pouches with the relative humidity between 50 and 70% before irradiation.
- Since the films are read optically, they should be kept free of dirt, scratches, and fingerprints.
- The films must be protected from UV irradiation at all times.
- In general, the films should not be read until approximately 24 h after irradiation, because the full dye development requires several hours.

Any dosimeter used to determine absorbed dose in an irradiated product has to be calibrated.[1,2] The adiabatic character of electron beam deposition is used in calorimetry, which is the primary absolute method of measuring the absorbed dose (energy per unit mass).[4] An example of the instrument for this purpose is the water calorimeter developed in Risø National Laboratory in Denmark.[11,12] This calorimeter is reported to be suitable for electrons from a linear accelerator with energies higher than 5 MeV and

shows an accuracy of ± 2%.[9] Other types of instruments for this purpose are the graphite calorimeter[13] and polystyrene calorimeter.[14] For example, a totally absorbing graphite body calorimeter is reported to be suitable for measuring energy-deposited electron accelerators operating within the range of 4 to 400 MeV.[15–17]

Essentially, a calorimeter measures absorbed dose in terms of the radiation-induced temperature rise in the calorimeter core connected electrically to the outside. The dose to the dosimeter being calibrated is related to the associated calorimeter reading of the net temperature rise. These calorimeters are used as reference dosimeters for high-energy electron beams (2–12 MeV) and also for small references and routine dosimeters (pellets and radiochromic films).

The calibration is done by national or secondary standards laboratories. Calibration at the National Institute of Standards and Technology (NIST) involves exposure to either gamma ray source ($^{60}$Co) over the dose range $10^0$ to $10^7$ Gy, or high-energy electron beam (1 to 28 MeV) combined with a graphite or water calorimeter.[1]

*Alanine dosimeters* are based on the ability of l-α alanine (a crystalline amino acid) to form a very stable free radical when subjected to ionizing radiation. The alanine free radical yields an electron paramagnetic resonance (EPR) signal that is dose dependent, yet independent of the dose rate, energy type, and relatively insensitive to temperature and humidity.[18] Alanine dosimeters are available in the form of pellets or films and can be used for doses ranging from 10 Gy to 200 kGy.[19] A reference calibration service using the alanine EPR system was developed and the scans were sent to the service center by mail. Currently the available system allows transferring the EPR scan to a NIST server for a calibration certificate. This way the procedure has been shortened from days to hours.[19]

Other instruments for evaluation of electron beam process are *real-time monitors*. They provide a continuous display in real time of dose delivered to product, as well as the energy of the electron beam. Moreover, they can show the variations in dose across a wide web if multiple detectors are installed and provide alarm signals to warn the operator of high- and low-dose conditions, and record the performance of the processor for production control, quality assurance, and maintenance needs. The major advantage of these real-time instruments is that they monitor the current and beam energy independently.[20,21]

## 9.2  UV Radiometry

There are several devices measuring either the number of photons (total or per unit time) or the amount of radiation converted into electric signal or into heat. These are *actinometers* and *radiometers.*

### 9.2.1 Actinometers

Actinometers are chemical systems or physical devices that determine the number of photons in a beam either integrally or per unit time. In a *chemical* actinometer, the photochemical change can be directly related to the number of photons absorbed, while the *physical* device gives a reading correlated to the number of photons detected.[22]

### 9.2.2 Radiometers

Radiometers are quantitative physical detectors of radiation, which convert the radiant energy to an electrical signal. They can be used for monitoring and controlling UV curing systems in order to produce the desired cure.

In their simplest form, radiometers monitor irradiance (in W/cm²) and radiant energy density (in J/cm²) for the bandwidth of the instrument. Profiling radiometers can in addition to that also provide irradiance profiles as a function of time. The results from the monitoring of a process can be effectively used to correlate exposure conditions to the physical properties of the cured product. If needed, they can also become the specifications of exposure in the design of production systems. Usually, radiometers are placed in the same position as the material that is being cured.

Some self-contained instruments are designed for on-line measurements in UV curing units to determine the integral UV dose delivered to the material being cured, peak irradiance, and irradiance/temperature profiles.[4] The quantities and units of measurements have been established based on IUPAC's recommendation of 1996.[22] These are listed in Table 9.3.

**TABLE 9.3**

Quantities and Units Related to UV Radiometry

| Quantity | Symbol | SI Unit | Common Unit |
|---|---|---|---|
| Irradiance | $E$ | $W\ m^{-2}$ | — |
| Photon exposure | $H_p$ | $m^{-2}\ mol\ m^{-2}$ | — |
| Photon flow | $\Phi_p$ | $s^{-1}\ mol\ s^{-1}$ [a] | — |
| Photon irradiance | $E_p$ | $m^{-2}\ s^{-1}$ | — |
| Photon flux | | $mol\ m^{-2}$ [a] | |
| Radiant energy | $Q$ | $J$ | — |
| Radiant power | $P$ | $W$ | — |
| Radiant exposure | $H$ | $J\ m^{-2}$ | |
| Spectral irradiance | $E_\lambda$ | $W\ m^{-3}$ | $W\ m^{-2}\ nm^{-1}$ |
| Spectral photon flow | $\Phi_{p\lambda}$ | $s^{-1}\ m^{-1}$<br>$mol^{-1}\ s^{-1}\ m^{-1}$ [a] | $s^{-1}\ nm^{-1}$<br>$mol^{-1}\ s^{-1}\ nm^{-1}$ [a] |
| Spectral photon flux | $E_{p\lambda}$ | $s^{-1}\ m^{-3}$ | $s^{-1}\ m^{-2}\ nm^{-1}$ |
| Photon irradiance | | $mol\ s^{-1}\ m^{-3}$ [a] | $mol\ s^{-1}\ m^{-2}\ nm^{-1}$ [a] |
| Spectral radiant power | $P_\lambda$ | $W\ m^{-1}$ | $W\ nm^{-1}$ |

[a] If the amount of photons is used.

**TABLE 9.4**

Examples of Radiometers for UV Measurement

| Instrument | Spectral Range, nm | Measuring Range[a] |
|---|---|---|
| UV intensity meters | 250–260 | 0–19 W/cm² |
| | 280–320 | |
| | 320–390 | |
| Spot cure radiometers | 250–445 | 0–19.99 W/cm² |
| Radiometers for xenon flash | 326–401 | 57 nW/cm² to 57 W/cm² |
| UV cure radiometers | 250–400 | 1 nW/cm² to 1 W/cm² |
| | | 150 nW/cm² to 0.5 W/cm² |
| | 250–290 | 0–20 m W/cm² |
| Handheld radiometers | 280–340 | 0–200 W/cm² |
| | 335–380 | 0–2,000 µW/cm² |
| | (Three sensors) | 0–200 mW/cm² |
| | 240–425 | Min. 10 nW/cm²/nm |
| | (in 1 nm steps) | Max. 10 W/cm² |

[a] Irradiance or spectral irradiance.

Depending on their function, radiometers can be either thermal or photon detectors. In *thermal detectors*, the incident photon energy is converted into heat, which is then measured. The measured data are independent of wavelength. *Photon detectors* are based on photoelectric effect and measure spectrum intensity. The results are dependent on wavelength.

Instrument manufacturers offer a variety of devices, including monitoring systems for standard process or for spot curing technology and systems for process control. More advanced systems "map" the entire process and evaluate the lamp focus, reflector focus, and reflector efficiency within a specific region, and compare spectral output, degradation, and uniformity of one or more lamps in multiple-lamp arrays. Such a system also measures and documents substrate temperatures during the entire process and tracks and stores data for statistical quality control, regulation compliance, or historical comparisons[23]; detects changes; and sounds the alarm when the UV drops below a set limit.[24] Examples of commonly used radiometers are listed in Table 9.4.

Radiometers are exposed to the UV source and provide the total energy (J/cm²) or UV peak irradiance (W/cm²) in absolute units. Depending on design, they provide data in one or four spectral bandwidths. They are used in all UV curing chemistries, including inks, adhesives, solder masks, and epoxies. Besides measuring the performance of a UV lamp, they compare the efficiency of curing systems and establish the UV level for proper curing. An example of a general purpose radiometer is in Figure 9.3

*Radiometers for spot cure* monitor the performance (irradiance), measure the light guide degradation, determine optimum positioning of the light guide cable, and compare the efficiency of spot curing systems. An example of a

**FIGURE 9.3**
Example of an absolute reading radiometer displaying four different bandwidths simultaneously. (Courtesy of EIT, Inc.)

spot cure radiometer is in Figure 9.4. A radiometer measuring both spot and flood cures is in Figure 9.5.

*Profiling radiometers* measure and display the peak power and total density ion of a UV curing system and also profile the temperature and irradiance as a function of time. The information is transferred into a computer. They are capable of comparing characteristics of multiple lamps, comparing UV systems over time, or comparing different systems to each other. They track and store archival data. An example of profiling radiometers is in Figure 9.6.

*Radiometers for three-dimensional cure* are used for simultaneous multipoint measurements, for setup and process verification of the lamp system. They can be used with UV lamps mounted on a fixed bank or a robotic arm. The collected exposure data (irradiance and total UV energy) are displayed on a computer for each sensor position. A 3DCure radiometer is shown in Figure 9.7, and an example of a screen display from a 3D radiometer in Figure 9.8.

*On-line monitoring equipment* provides continuous monitoring of UV lamp intensity. Results are displayed as a percentage of the original output, which
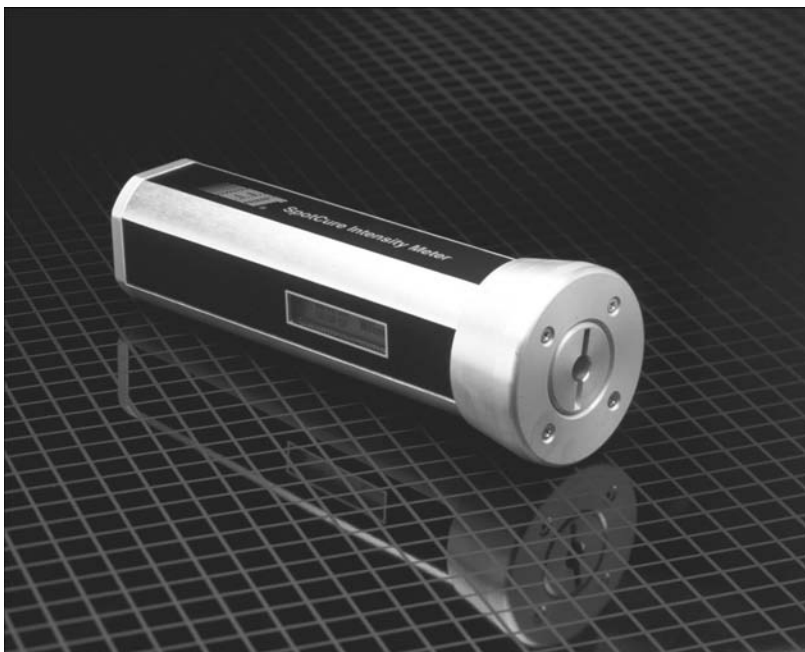
**FIGURE 9.4**
Monitor for spot curing. (Courtesy of EIT, Inc.)

is usually set at 100%. Equipment with compact sensors for monitoring is shown in Figure 9.9.

*Probes* (example shown in Figure 9.10) are used for applications where space is limited or difficult to access. They are capable of establishing and maintaining process window and coordinate readings from on-line displays.

Equipment manufacturers suggest sensor locations as shown in Figure 9.11. However, since lamps vary in design and installation, these locations may in some cases be different.

### 9.2.3  Radiochromic Films

Radiochromic films are used routinely in the measurement of EB doses in the form of cellophane strips or tabs that attach to the surface of the irradiated web or part (see Section 9.1), but can also be used in the UV curing process.[25] They respond to total time-integrated energy by changing color or optical density, typically in the wavelength range from 200 to 350 nm, without any wavelength specificity. Their advantage is that they can pass through the UV system, including nips of rollers, without being damaged. Their drawback is that they respond and record accumulated energy only and cannot distinguish between exposures of individual lamps if used in multilamp systems.
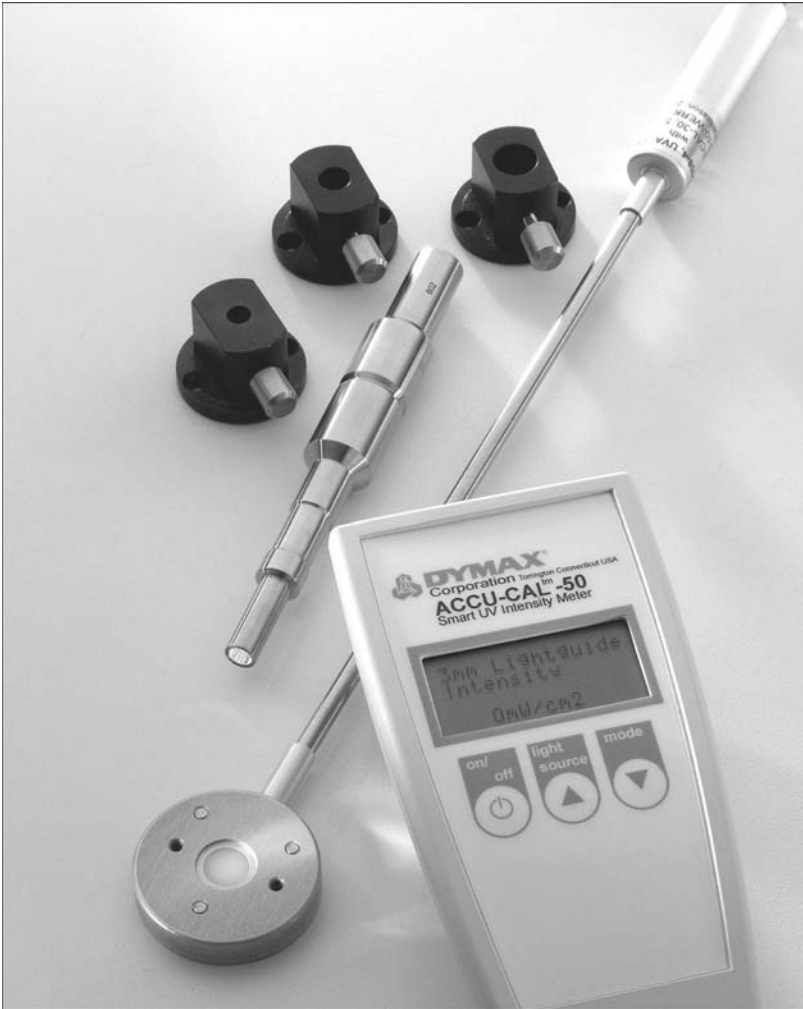
**FIGURE 9.5**
Radiometer for spot and flood cures. (Courtesy of Dymax Corporation.)

Obviously, the user has a large selection of instruments, each of them having a different function. The selection depends on what the user wants to measure and for what purpose.

In *process design*, the main objective[26] is to optimize the cured properties of the finished product. To that end, the following conditions have to be established and quantified:

- Effective irradiance or profile
- Spectral distribution
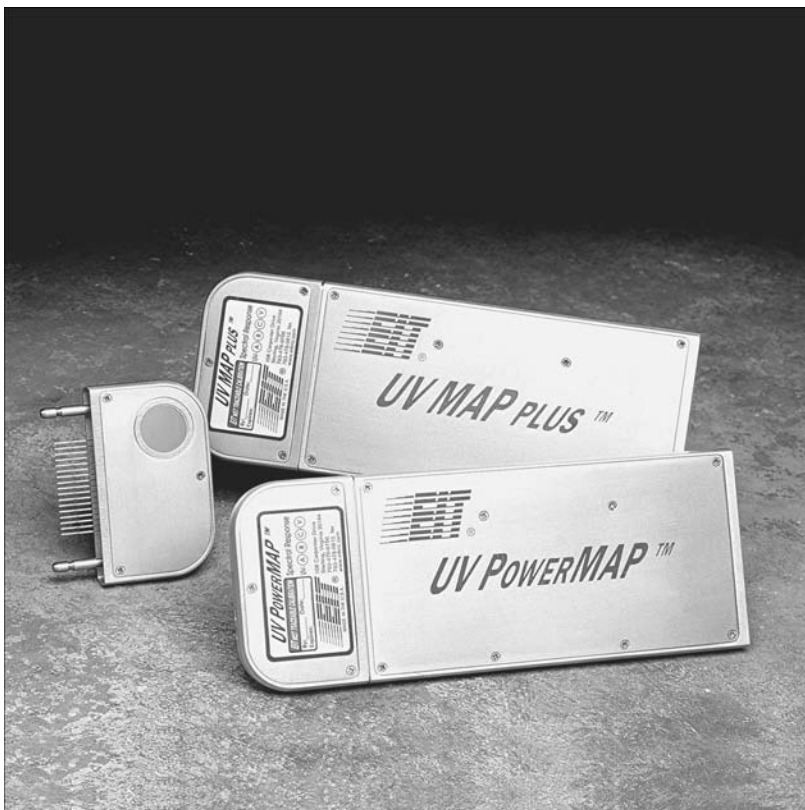
**FIGURE 9.6**
Profiling radiometers. (Courtesy of EIT, Inc.)

- Time or speed (to determine energy)
- Amount of infrared energy or temperature

Thus, these measurements provide quantitative information about the critical parameters used in the process, and help establish the limits within which the process is successful, or the so-called process window.

Once the process window is established, the goal is to maintain the operating condition within the established limits. This is often referred to as *process control.* The primary purpose of process control is to monitor the process to get a feedback by means of on-line radiometric measurements and take action to keep it within the established limits. Process monitoring has to verify that the key process variables remain within the specified limits, and to interpret changes in the exposure conditions to help maintain control. Once established, proper measurements are invaluable in monitoring the condition of the UV lamps and determining when they have to be maintained or replaced.[4]

**FIGURE 9.7**
Radiometer for 3DCure. (Courtesy of EIT Inc.)
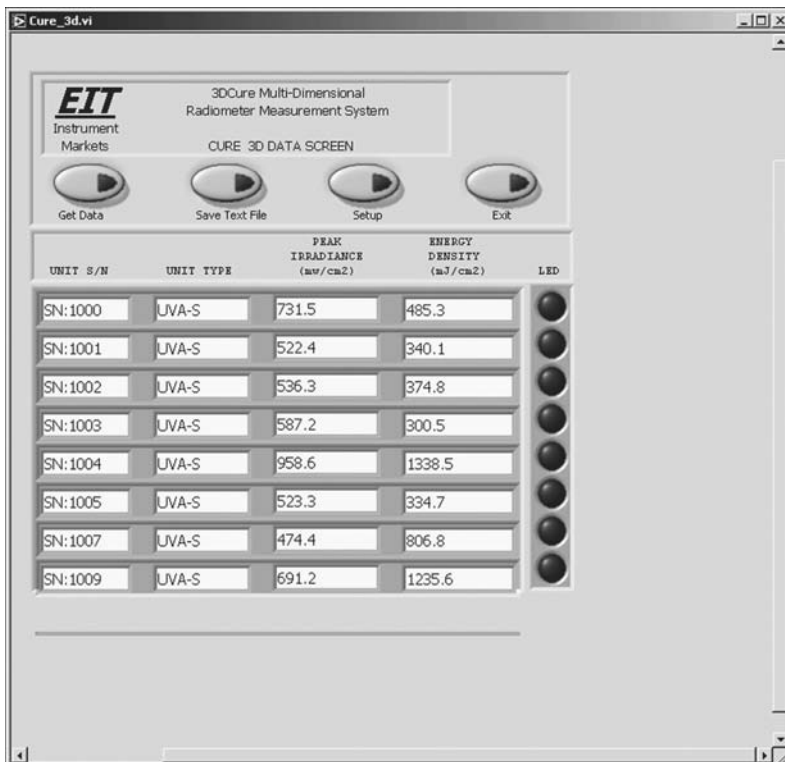


**FIGURE 9.8**
Display from 3DCure radiometer. (Courtesy of EIT, Inc.)

**FIGURE 9.9**
On-line monitoring instrumentation. (Courtesy EIT, Inc.)



**FIGURE 9.10**
Probe for production ambient light measurement. (Courtesy of EIT, Inc.)
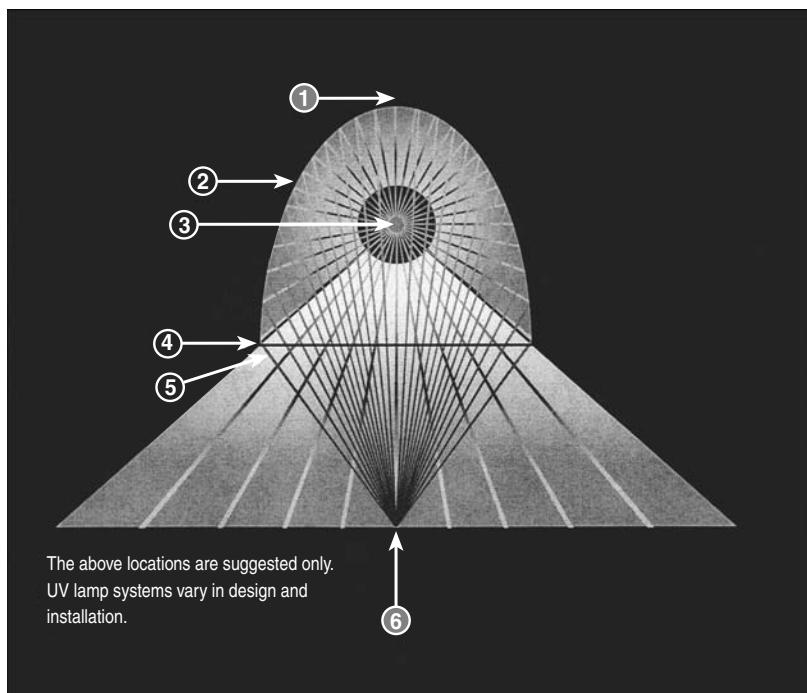
**FIGURE 9.11**
Suggested sensor location. 1, behind reflector near end of bulb; 2, behind reflector looking at bulb and reflected energy; 3, from end of lamp housing; 4, through filter material or rod; 5, looking up at bulb and reflector from below; 6, directly under the lamp at substrate level. (Courtesy of EIT, Inc.)

Certain processes, such as 3D curing, roll-to-roll printing and coating, and jet printing, are difficult or even impossible to evaluate by the use of traditional radiometry. On the other hand, radiochromic films exhibit a change of hue with exposure, changing their optical density in a specific color component, but cannot resolve irradiance or any information on the irradiance profile of exposure. An advanced study to solve some of the problems by evaluating methods of correlation to produce a numerical measure of UV exposure was performed. The principal purpose of this study was to explore the use of standard instruments to quantify the response of radiochromic films in terms of transmission or reflection densitometry. It concluded that several radiochromic films have a wide dynamic exposure range, good linearity, and nearly perfect cosine response, are economical, and can be read with comparatively inexpensive instruments. This allows correlation of their optical density with instrument radiometry for process design optimization or periodic measurements to verify lamp condition over time. The important conclusion was that, when carefully designed and used, radiochromic films can be a useful extension of—but not a substitute for—instrument radiometry.[27]

The subject of EB and UV dosimetry is discussed thoroughly in Mehnert et al.[4] The most recent discussion of radiometric methods for UV processing was by J. Raymont, "UV Measurement and Process Control," UV/EB West 2009 Conference, February 17–18, 2009, Los Angeles (RadTech International, North America).[28]

A comprehensive coverage of main instrumentations for UV radiation measurements is in *Radiometers*, Document 100200, CAT REV B 305 (EIT Instrument Market, Sterling, VA).

## References

1. McLaughlin, W. L., and Desrosiers, M. F., *Radiat. Phys. Chem.*, 46, p. 1163 (1995).
2. Humphreys, J. C., and McLaughlin, W. L., *IEEE Trans. Nucl. Sci.*, NS-28, p. 1797 (1981).
3. ASTM Standards E170, E668, E1026, E1204, E1261, E1275, E1276.*
4. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV and EB Technology and Equipment*, Vol. 1, John Wiley & Sons, Chichester/SITA Technologies Ltd., London, p. 107 (1998).
5. Janovsky, I., and Mehta, K., *Radiat. Phys. Chem.*, 43, p. 407 (1994).
6. Mc Laughlin, W. L., Puhl, J. M., and Miller, A., *Radiat. Phys. Chem.*, 46, p. 1227 (1995).
7. Abdel-Fattah, A. A., and Miller, A., *Radiat. Phys. Chem.*, 47, p. 611 (1996).
8. McLaughlin, W. L., *Radiat. Phys. Chem.*, 67, p. 561 (2003).
9. Zagórsky, Z. P., in *Radiation Processing of Polymers* (Singh, A., and Silverman, J., Eds.), Carl Hanser Verlag, Munich, p. 279 (1992).
10. Rangwalla, I., and Swain, M., *RadTech Report*, 17, No. 5, September/October, p. 26 (2003).
11. Brynjolfsson, A., and Thaarup, G., *Rep. Riso*, 53, Risø National Laboratory, Denmark (1963).
12. Holm, N. W., and Berry, R. J., *Manual on Radiation Dosimetry*, Marcel Dekker, New York (1970).
13. McLaughlin, W. L., Walker, M. L., and Humphreys, J. L., *Radiat. Phys. Chem.*, 46, No. 4–6, September, p. 1235 (1995).
14. Miller, A., Kovacs, A., and Kuntz, F., *Radiat. Phys. Chem.*, 46, No. 4–6, September, p. 1243 (1995).
15. McLaughlin, W. L., et al., *Dosimetry for Radiation Processing*, Taylor & Francis, London (1989).
16. Sunaga, H., et al., *Proceedings of the 6th Japan-China Bilateral Symposium on Radiation Chemistry*, Waseda University, Tokyo, Japan, November (1994).
17. Janovsky, I., and Miller, A., *Appl. Radiat. Isot.*, 38, p. 931 (1987).
18. Garcia, R. M. D., et al., *Radiat. Phys. Chem.*, 71, p. 373 (2004).
19. *e-scan™ Alanine Dosimetry System*, Brochure, Bruker Biospin, GmbH, www.bruker-biospin.com.
20. Kneeland, D. R., Nablo, S. V., Weiss, D. E., and Sinz, T. E., *Radiat. Phys. Chem.*, 55, p. 429 (1999).

21. Korenev, S., Korenev, I., Rumega, S., and Grossman, L., *Radiat. Phys. Chem.*, 71, p. 315 (2004).

22. Commission on Photochemistry, Organic Chemistry Division, International Union of Applied Chemistry, *Pure Appl. Chem.*, 68, p. 2223 (1996).

23. Braun, A. M., Maurette, M. -T., and Oliveros, E., *Photochemical Technology*, John Wiley & Sons, Chichester, p. 51 (1991).

24. *Guide to UV Measurement: Technology, Radiometry and Measurement for Industrial UV Curing*, RadTech International North America, Chevy Chase, MD, www.radtech.org.

25. Diehl, D., and Abbe, P., *RadTech Report*, 14, No. 1, January/February, p. 14 (2000).

26. Stowe, R. W., *Technical Conference Proceedings, RadTech 2002 North America*, Indianapolis, IN, April 28–May 1, p. 475 (2002).

27. Stowe, R. W., and Guarniere, J. W., *Technical Conference, RadTech North America*, Chicago, May 4–7 (2008).

28. Raymont, J., UV/EB West 2009 Conference, February 17–18, 2009, Los Angeles, CA, Radtech International, North America.

* ASTM Standards E1204, E1261, E1275, and E1276 were replaced by Standards ISO/ASTM51204, ISO/ASTM51261, ISO/ASTM51275, and ISO/ASTM51276, respectively.

# 10

## Safety and Hygiene

Ultraviolet and electron beam technology has been recognized as a process successfully using low or zero content of volatile organic compounds (VOCs) for more than 25 years. This is a very important advantage over traditional processes in coating, printing, and adhesive applications using organic solvents and other volatile ingredients exclusively. However, as with any industrial manufacturing process, there are disadvantages and some hazards due to equipment, procedures, and raw materials used. In UV/EB curing, these hazards are attributable to reactive chemicals, some volatiles, and the nature of the energy sources.

Ultraviolet energy used in the curing process is a nonionizing or *actinic* form of electromagnetic radiation. The energy level is not high enough to penetrate into the human body and interact with the tissues causing cell damage, as do other forms of radiation. However, a direct exposure to UV light can have effects on both skin and eyes.

Electron beam processors generate two types of *ionizing* radiation: their primary product is high-energy electrons, and their secondary product is x-rays resulting from their interaction with matter. The ionizing radiation is damaging because of its capability of penetration into the human body.

The radiation curable liquid systems consist of a variety of chemical compounds, some of which may pose hazards due to their toxicity or tendency to irritate skin or eyes.

## 10.1 UV Equipment Health and Safety

The biological effects of UV radiation result mostly from exposure to wavelengths below 325 nm and resemble the typical syndromes of sunburn, such as skin reddening (erythema), skin burning, dryness, premature aging, and pigmentation. Eyes may be also affected by developing inflammation, pain, photophobia, tearing, temporary blindness, and cataracts.[1] The eyes are most sensitive to UV radiation from 210 nm (UVC and UVB). Maximum absorption by the cornea occurs around 280 nm. Absorption of UVA in the lens may be a factor in producing cataracts (clouding of the lens in the eye). Acute overexposure of the eye to UV radiation can cause photokeratitis (inflammation of the cornea) and photoconjunctivitis (inflammation of the cornea, more commonly

known as "snow blindness" or "welders' flash"). Symptoms range from mild irritation to severe pain and, in an extreme case, to irreversible damage.[2]

Industry exposure limits for UV light, established by government agencies, are:[1]

- Near UV (315–400 nm): 1 mW/cm$^2$ for exposures longer than 16 min
- Actinic UV (200–315 nm): 0.1 mW/cm$^2$ for an 8 h exposure

Hazards due to exposure can be minimized by sound basic engineering, administrative, and hygiene controls. The curing equipment should be properly shielded to prevent escape of UV light into workplace. Personnel working in the UV curing area should wear special protective eyewear. Access openings to the UV curing equipment should be interlocked to ensure that the radiation source is turned off when the shield is removed. Commercial instruments are available to monitor UV light in the workplace.[2] The Occupational Safety and Health Administration (OSHA) has a standard that covers employee exposure to radiation, *Nonionizing Radiation* (29 CFR 1910.97), and copies of that standard are available from http://www.osha.gov. Other standards are available from the American Conference of Governmental Industrial Hygienists (ACGIH), which has recommended workplace exposure limits and updates, threshold limit values for chemical substances and physical agents, and biological exposure indices in their ultraviolet radiation section.[2]

The Canadian Centre for Occupational Health and Safety (CCOHS) publishes a web page for comprehensive discussion of guidelines for occupational exposure to UV light and safe practices at http://www.ccohs.ca/osha answers/phys_agents/ultraviolet radiation.html.

Another potential hazard is exposure to ozone, which is generated by most UV lamps, particularly at wavelengths below 200 nm. This colorless gas has a characteristic strong smell and can therefore be detected already at concentrations below its acceptable workplace limit of 0.1 ppm. It will cause biological effects, such as headache, fatigue, dryness of the upper respiratory tract, pulmonary irritation, and may also contribute to respiratory infections.[3] Most UV curing operations use air as the curing atmosphere; consequently, the generation of ozone is a common occurrence. Therefore, the equipment should have ozone filters and sufficient exhaust to prevent escape of ozone and other volatiles into the workplace. The current ACGIH threshold limit value (TLV) ceiling for ozone is 0.1 ppm. The odor threshold concentration is about 0.01–0.02 ppm, so ozone is detectable by odor before dangerous concentrations are reached.[2] Engineered exhaust systems normally are adequate to prevent escape of ozone into the workplace; however, ozone levels should be monitored regularly to ensure compliance with safe workplace concentrations.[2]

Since the majority of UV lamps generate an appreciable amount of heat, there is a hazard of burning when touching the lamps or certain parts of the equipment. This hazard can be minimized by proper equipment design and by adequate air or water cooling of reflectors, lamp housings, and shutters, and by placing aluminum plate heat sinks below the lamp and the substrate.[4]

Most UV equipment operates at voltages well above the main level, and it is important to prevent exposure to high voltage by proper installation. Microwave-powered lamps have a microwave detector to detect microwave radiation leakage. The system is shut down when microwave irradiance of 5 mW/cm² is detected.[4]

With current technology, the use of mercury is crucial in achieving the required light output for practical UV curing lamps, and for the necessary lamp efficiency and long lamp life. However, mercury is a toxic element, requiring training in safe use and compliance with strict regulations concerning its disposal. The applicable regulations as well as safe practices of disposal of used lamps are listed in some detail in the literature.[2]

## 10.2 EB Equipment Health and Safety

As mentioned earlier, the stoppage of fast electrons generates x-rays, which are hazardous to human health. X-rays cause cell damage that can lead to cancer formation or genetic mutations. Even at small dosages, x-ray exposure may cause skin burning and general radiation syndrome.

Manufacturers of electron beam equipment provide adequate shielding. The thickness of the shielding and the material used for it depend on the accelerating voltage. Typically, 1 in. (25 mm) thick lead shielding is capable of stopping any x-rays generated by 300 keV accelerators. Most lower-voltage electron beam processors are self-shielded, which means that the electron (and x-ray) source is completely enclosed by shielding. Removable parts of the shielding have been equipped by safety interlocks so that the high voltage of the accelerator is turned off when the shielding is opened. EB units are provided with a radiation detector, which automatically shuts down the power if an alarm setting is exceeded.[1] Units with higher accelerating voltages, typically above 600 keV, require separate vaults constructed from concrete, steel, or a combination of them, enclosing the equipment. State and local governments have regulations controlling the use of radiation-producing equipment, and all electron beam units must be licensed.

The current federal guidelines for occupational exposure to ionizing radiation in the United States are in the Code of Federal Regulations, Part 1910.96. They stipulate that personnel working in the area where ionizing radiation is produced should not receive in any period of a calendar quarter more than the following dose equivalents (rem):[5]

- Whole body, head and trunk, active blood-forming organs or gonad          1.25
- Hands and forearms          18.75
- Skin or whole body          7.5

Employees working in the area where EB equipment is operating must be monitored for exposure to ionizing (mainly x-ray) radiation with film badges, which detect and quantify any exposure to stray radiation. The employers must train workers thoroughly in the operation of the equipment and proper safety and hygiene, and keep records of exposure of their personnel to ionizing radiation. OSHA has a standard that covers employee exposure to radiation, *Ionizing Radiation* (29 CFR 1910.1096), and copies of that standard are available from http://www.osha.gov.

## 10.3 Chemical Hazards

Materials used in UV/EB curing may present mainly hazards in skin and eye contact and, to a lesser degree, due to accidental ingestion. In some operations, where spray equipment is used, there is some possibility of inhalation of volatilized materials.

Acrylate types of monomers and oligomers are known to be skin and eye irritants. Even if they do not cause irritation immediately, they may sensitize a person over a longer exposure and cause allergy.[6] On the other hand, they represent much less of a hazard than common solvents (see Table 10.1).

Recently, there has been an issue with the detection of 4-methylbenzophenone (MBP) in breakfast cereal in Europe, leading to publicity concerning the presence of this photoinitiator in the food. Based on the close similarity between MBP and benzophenone, a photoinitiator for inks and coatings that are cured with UV light, the European Food Safety Authority (EFSA) has concluded that short-term consumption of breakfast cereals containing ppm traces of MBP should not pose a risk to most people, but recommended that this substance undergo more detailed evaluation if it will continue to be used in food packaging.[7]

**TABLE 10.1**

Comparison of the Toxicity and Other Properties of UV/EB Curable Systems with Common Solvents

| Chemical | Flash Point, °F | VOC | Hazardous Waste | Systemic Skin Irritant | Toxicity | Reproductive Effects |
|----------|-----------------|-----|-----------------|------------------------|----------|----------------------|
| TMPTA | >212 | No | No | Yes | No | No |
| Oligomer | >>212 | No | No | Maybe | No | No |
| VM&P Naptha | <0 | Yes | Yes | Yes | Yes | No |
| Toluene | 40 | Yes | Yes | Yes | Yes | Yes |
| Xylene | 100 | Yes | Yes | Yes | Yes | Yes |
| 1-Butanol | 100 | Yes | Yes | Yes | Yes | Yes |

*Note:* TMPTA = trimethylolpropane triacrylate.

There are many aspects of protection of personnel handling the chemicals in a production setting. First, they must be informed about the hazards involved by reading thoroughly the material safety data sheet (MSDS) for each material used. These must be supplied by the manufacturer or vendor of the chemical and must be accessible to the personnel at all times. MSDSs not only inform about the hazards, but also recommend proper handling, the type of personal protection to be used, ways of disposal, ways to handle spills, and emergency contacts.

Skin should be protected by gloves (preferably nitrile or butyl rubber), boots, and long-sleeve clothing. For the protection of eyes, safety glasses with side shields or splash goggles are the best choice when handling liquid chemicals. If spray equipment is used, proper respiratory protection may be needed. If any contact with the chemical occurs, the affected area has to be washed with soap and water immediately; solvents should not be used. In extreme cases, proper medical help may be required.

In the European Union, a very comprehensive initiative with the aim to improve the protection of human health and the environment from the hazards of chemicals, and to enhance the competitiveness of the EU's chemical industry, is under way. It is referred to as REACH, which stands for Registration, Evaluation, Authorization, and Restriction of Chemicals. REACH places greater responsibility on industry to manage the risk of chemicals and provide appropriate safety information to professional users and, as far as the most hazardous substances, to consumers. New substances need to be registered before they are placed on the market. REACH came in force on June 1, 2007, with a phased implementation over the next decade.[8] There is no doubt that it will affect the UV/EB industry.

## References

1. Golden, R., *RadTech Report*, 11, No. 3, May/June, p. 13 (1997).
2. *Ultraviolet Curing Lamp Safety and Handling*, RadTech (The Association for UV&EB Technology), Bethesda, MD.
3. *UV/EB Curing Primer 1*, 4th ed., RadTech International North America, Northbrook, IL, p. 55 (1995).
4. Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV & EB Technology and Equipment*, Vol. 1, John Wiley & Sons Ltd., Chichester/SITA Technology Ltd., London, p. 269 (1998).
5. *UV/EB Curing Primer 1*, 4th ed., RadTech International North America, Northbrook, IL, p. 57 (1995).
6. Bean, A. J., and Cortese, J., *FLEXO*, 25, No. 7, July, p. 37 (2000).
7. *4-Methylbenzophenone*, RadTech briefing, update March 13 (2009).
8. European Commission, Joint Research Centre, Institute for Health and Consumer Protection, June (2009).

# 11

## Recent Developments and Trends

The key industry drivers are based mainly on cost reduction, reduced energy consumption, and environmental issues. The main components of economy where UV/EB technology has been growing are:

- Vehicle building (automotive plastics and composites, wiring and cable coatings, and paints, electronics, adhesives, and fuel cells) and automotive refinishing
- Aerospace (wiring and cables, composites, adhesives, repairs, and marking)
- Housing and construction (wood structures, flooring, furniture, laminates, composites, displays, wiring and cables, and optical fibers)
- Electronics and electrical (wires and cables, shrinkable tubing, displays, conformal coatings, adhesives, and battery separators)
- Medical (coatings, adhesives, sensors and probes, prosthetics and biomedical products, and optical fibers)
- Consumer products (packaging, shrinkable films and sheets, labels, displays, and CDs and DVDs)
- Other (protective coatings, adhesives, shrinkable tubings, displays, and composites)

## 11.1 Current Trends in Equipment and Chemistry

The main drivers for both equipment and chemistry are cost reduction, energy reduction, and environmental issues (sustainability, "green" raw materials, reduced volatile organic compound (VOC), reduced toxicity, lowering odor, reduced defects and manufacturing scrap).

Companies are increasingly considering sustainability in their business decisions.

UV/electron beam (EB) technology offers several sustainability features when compared to thermal curing:

- Reduced use of solvents or their complete elimination
- Reduced usage of energy
- Safer workplace
- Reduced usage of fossil fuels and reduced greenhouse gas emissions
- Reduced or entirely eliminated pollution controls
- Reduced transportation costs due to reduced or eliminated consumption of solvents
- Recyclable inks, coatings, and product wastes

These features have a positive influence on performance and economic returns.

**NOTE:** The World Commission on Environment and Development defines *sustainability* as "development that meets the need of the present without compromising the ability of future generations to meet their needs."

### 11.1.1  UV/EB Equipment

The sizes of equipment and its components continue to be reduced to become less costly and consume less energy. Tendencies are to make them portable and modular where possible. Other trends are:

- Growth of the use of robotics
- Growth of 3D curing (both UV and EB)
- Enhancing safety

For more on recent developments in equipment see Section 3.2.2.

### 11.1.2  Chemistry

In chemistry, the main efforts are geared toward improvement of the environmental impact by reducing VOC and using either aqueous resins or resins without any VOC or water. Automotive OEM production and the refinishing business are demanding a highly weather- and scratch-resistant top coat with no or minimal possible yellowing, improved bonding between individual coatings and paint, as well as dependable dual-cure systems for shadowed areas. In general, further development of fiber-reinforced polymeric composites and gel coats (both UV and EB) is under way for many industrial and consumer products. New monomers and oligomers based on natural and sustainable raw materials are being developed. Relatively numerous applications of nanotechnology are emerging.

## 11.2 Emerging Technologies and Applications

Below are some novel applications. Because the number of them grows at a great rate, these only represent a "snapshot" taken at this writing, and the list is far from being complete.

### 11.2.1 Composite Processing and Repairs

The main potential for expansion of UV/EB into aerospace and certain commercial applications is by developing radiation curing of polymeric fiber-reinforced composites. The initial work on composite skin repairs involve applying the UV curing technology with bisacryl phosphine oxide to ensure the cure of relatively thick layers. A total of ten layers were used at a time. The UV cured composites closely matched those produced by heating.[2]

An alternative is a cationically initiated epoxy resin system cured by electron beam. The experiments with this process showed the following advantages:

- Reduced residual stresses
- Considerably shorter curing times (minutes vs. hours)
- Improved material handling (unlimited shelf life of the resins at ambient temperatures
- Possibility of process automation (fiber placement)

Also, EB curable adhesives aluminum to aluminum, graphite to aluminum, and graphite to graphite were used successfully.

The repairs were performed on lower- and upper-wing skin assemblies and on a composite liquid hydrogen tank. On average, they took 50–70% of the time required for a normal thermal repair.[3] The only process where EB cannot be used is resin transfer molding (RTM) because the electrons cannot penetrate the thick steel tooling required for it. The typical dose for this process was found to be 100 kGy.[3]

On-aircraft repairs of composite using a rapid-cure resin system of composite component with UV light irradiation based on TRI patent[4] have been developed by the U.S. Air Force Research Laboratory. Alternating layers of the acrylate-based resin system and woven fiberglass (the widely used wet layup procedure) are applied to fill the hole and form a UV curable composition.[5] The width of the patch can be up to 2 ft (0.6 m) and the depth as much as 0.2 in. (5 mm). The cure time using a 400 W UVA lamp is reported to be 20 min.[5] Although it is essentially a depot repair, it can be done field when necessary to return an aircraft to service. Because of the necessity to cure relatively thick repair patches, *bis-acylphosphine oxide* was used as a photoinitiator.[5] An example of the patented UV curable resin system used for the repairs is in Table 11.1.

**TABLE 11.1**

Example of a UV Curable Formulation for Composite Repair

| Component | Function | Wt.% |
|---|---|---|
| Epoxy methacrylate | Oligomer | 30.00 |
| ISOTRI[a] | Monomer | 26.80 |
| Isobornyl methacrylate (ISBM) | Monomer | 16.75 |
| Methyl methacrylates (MMAs) | Monomer | 10.05 |
| Methacrylic acid (MA) | Monomer | 13.40 |
| Acylphosphine:phenyl ketone 1:3 | Photoinitiator | 3.00 |
| Total | — | 100.00 |

[a] Tris(2-hydroxyethyl) isocyanurate triacrylate.

Application of UVA cure to battlefield rapid repair of composites was discussed by Dworchak at the UV/EB West 2009.[6]

Another repair method is using curing by means of EB or x-rays. A practical system developed by Air Canada Maintenance Base in cooperation with Lockheed and Atomic Energy of Canada Ltd. is using EB curing for repair of the fiberglass wing to body fairing panels.[5] A rather comprehensive report on EB cure in industrial applications to composite materials is that of Saunders et al.[7]

Additional studies of the effects of EB cure on the properties of cured epoxy resin systems were done by Nitshitsui et al.[8] and Raghavan.[9]

### 11.2.2 UV Curable Concrete Coatings

UV curable concrete coatings have been recently developed.[10] They have low viscosity (about 150 mPa.s) to allow air release upon applications of 1–7 mils (0.25–1.8 mm) thick coating. The photoinitiators have been chosen so that the surface and thorough curing is ensured. Currently polyester acrylate oligomers are the best choice for concrete floors. Flow, leveling, and wetting agents may be necessary for the appearance of the coating. A starting formulation for such a coating is in Table 11.2.

The coating is applied by traditional trade practices, namely, using rubber squeegees and paint rollers. The applied coating is cured by a mobile curing unit, which consists of a cart housing power supply for the UV lamp (see Figure 11.1).[11] If the concrete is porous, a seal coat should be applied (aqueous UV curable polyurethane dispersion (PUD) is recommended).

### 11.2.3 Wood Finishing

The majority of water-based UV systems are currently being used in the cabinet industry. Water-based UV coatings should be a blend of different resin systems; such blends offer certain benefits. Urethane systems offer excellent clarity, hardness, and flexibility. Acrylic resins are easy to apply and offer quick water evaporation.

**TABLE 11.2**

Example of a Starting Formulation for a UV Curable Concrete Coating

| Ingredient | Parts |
|---|---|
| Oligomers for desired coating properties | 30 |
| Oligomers for surface cure | 20 |
| Monomers for properties | |
| Multifunctional | 30 |
| Monofunctional for adhesion and viscosity reduction | 20 |
| Photoinitiator package | |
| Surface cure | 1–2 |
| Multipurpose | 2–4 |
| Through cure for thick coating | 0.25–0.50 |
| Amine synergist for surface cure | 2–5 |
| Additives | |
| For flow and leveling | 0–1.0 |
| For substrate wetting | 0–2.0 |
| Defoaming | 0–1.0 |

Water-based UV systems are gaining the most acceptance where the finishing must look like a traditional lacquer or varnish. Most water-based UV finishes contain 30–35% solids. Currently, it appears that the optimum UV system is a combination of a 100% solids system and water-based system on many wood products. One hundred percent solids finishes are used for sealing and filling the wood. When the wood is filled or sealed as desired, it can be cured and immediately sanded. Then the water-based UV system is applied to get the traditional look without the VOCs and in fewer steps than a traditional wood finish.[12]

Waterborne UV curable polyurethane dispersions have been developed that yield excellent performance when tested for exterior weathering. They
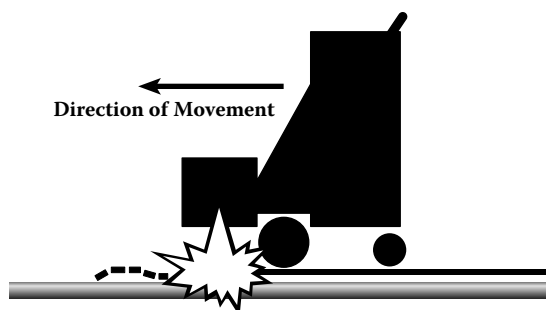


**FIGURE 11.1**
Schematic of a UV curing unit. (Weissmann, P. T., *RadTech Report*, 23, No. 1, RadTech International N.A., p. 24, 2009. With permission from RadTech International N.A.)

have high solids content (39–50%) and are solvent-free. They exhibit very fast water release and are suitable for clear and pigmented coatings.[12] They perform well on wood, plastics, leather, decorative film, and sheeting.[13]

### 11.2.4 Other

The use of UV-polymerized, vacuum-deposited film[14] has enabled the development of multilayer barrier coatings for thin-film photovoltaics and flexible electronics. The patented system uses thin polymer layers that are deposited alternatively with thin barrier layers. The multilayer structure is composed from organic (polymer) and inorganic (oxide) layers.

The polymer layer, typically between 250 and 1,000 nm thick, is deposited by flash evaporation of a multicomponent proprietary UV curable acrylate-based resin system. The requirements for the deposited film are:

- High transparency throughout the visible spectrum
- Low shrinkage (less than 15%)
- Low water solubility
- Low-term stability against UV degradation (weatherability)
- High interfacial adhesion for sufficiently high mechanical performance
- Structural stability at elevated temperatures and high humidity (i.e., 85°C and 85% relative humidity for a minimum of 2,000 h)

In addition to the thin-film solar cells, this system is suitable for use in other flexible electronics, such as a flexible, transparent, and light-weight encapsulation of organic light-emitting diode (OLED) displays and lighting.

*Factory-applied UV curable coatings*[15] have recently been developed for the building industry; they are available in a wide range of colors and are designed to be used in manufacturing plants. They can be applied by using vacuum, spraying, roll coating, and other common coating methods. The coating is then subjected to intense UV light, which cures it almost immediately. This can be done as a part of an in-line or off-line process.

The products coated by using this technology are:

- *Composites*, used mainly for decks, fences, and railing products. They are produced by blending a variety of materials (e.g., plastics and woof flour). The new type of coating can be applied directly to the products, although in some cases they must be surface treated, by usual methods, such as fluoro-oxidation, plasma, corona, or flame.
- *Fiber cement siding*, which is produced from a blend of cement, sand, and cellulose fibers. This blend is extruded into board, which is then cured by pressurized steam. Unlike composites, fiber cement siding does not require surface treatment. Normally, a primer is applied first, followed by another coating to achieve the desired color.

Frequently the material is only primed and the coating is applied later to meet requirements of the builder or distributor.

- *Vinyl products*, such as siding, fencing, and trim, are made from a typical compound containing PVC resin, stabilizers, UV inhibitors, processing aids, pigments, and plasticizers. The parts are extruded on standard extruders for plastics. Special UV curable coatings have been developed for vinyl building materials. The extruded profile is fed into a coating chamber, where any color coating can be applied. From there it is fed into a UV curing cabinet. In some cases only clear protective coating is used.

*Novel, UV curable nanotechnology coatings.*[16] These coatings are based on low-molecular-weight polymers (acrylics, epoxies, and polyurethanes) combined with monomers or oligomers. No solvents (VOC or water) are used. The formulations contain nanoparticles that may be silicon dioxide, aluminum oxide, or titanium dioxide. The use of nanoparticles produces substantial barrier properties. Formulations have been designed that can be applied onto most common substrates, including metal, glass, paper, and plastics.

Typical applications for these coatings are:

- Packaging and labels
- Electronics (consumer electronics substrates, protective coatings for transparent display surfaces, photovoltaic displays)
- Metal and plastics combinations (the combined products can be coated and cured in the same operation)
- Provision of corrosion and humidity resistance on metal products
- Writable metal surfaces (clear or colored surface that can be written on with a marker, pen, or pencil)

*Improved heat-resistant UV compositions for optical fiber applications.*[17] These compositions are nonurethane UV cure compositions that have neither carbamate moieties nor long-chain poly(alkylene oxide) soft segments and exhibit inherently better thermal stability measured by thermogravimetric analysis (TGA) than typical coatings for optical fibers based on urethane acrylate oligomers.

*UV curable flexo ink for RFID antennas.*[18] Radio frequency identification (RFID) devices and contactless smart cards are capable of uniquely identifying an individual or object when they are interrogated by an external radio frequency signal. Recently, a process of printing with the use of UV curable conductive flexo inks has been introduced. The inks are based on polyfunctional acrylates with silver flakes added for the electrical conductivity. The advantages of these inks are:

- Can be easily applied by flexographic printing
- Are high-solids systems
- Have a rapid cure

The shortcoming of these inks is that they can only be printed on nonporous substrates, since the binder absorption would prevent curing.

*Bioligomers.*[19] Bioligomers are acrylate oligomers containing renewable resources in their building blocks. They are used in lithographic inks. They offer the following advantages:

- Increased use of renewable resources
- Lithographic inks with good ink properties—tack, misting, reactivity, and printability
- Overprint varnishes with high gloss, reactivity, and solvent resistance

The oligomers contain 10 to 62% materials based on renewable resources.

*Aircraft markings.*[20] U.S. Air Force aircraft are painted in special hangars, and markings are often the bottleneck in getting aircraft out of the painting hangar; it can be up to 72 h from paint to fly. The paint is cured by UVA radiation.

*UV light-emitting diode (LED) lens technology.*[21] This technology is attractive for many materials processing and inspection applications. The LEDs are a solid-state light source that has a narrow optical spectrum and is energy efficient, rugged, and reliable. In addition, they can be built into environmentally friendly, mercury-free, and RoHS-compliant light sources for industrial applications. Due to the modular nature of LEDs and lens combinations, they can be readily scaled for large-scale application where mercury lamps or EB equipment would be used.

*Dual-cure resins for wood composites.*[22] These resins (heat and EB irradiation systems) are based on urethane-acrylate thermoplastic adhesive demonstrate efficacy to bond wood. Low amounts of EB radiation were needed to produce a wood bond that survived shipping and that improved the composite modulus. The system demonstrated promise and a new direction for wood adhesives.

*Energy curing of flexo inks on biopolymer films.*[23] Polylactic acid (PLA), a truly biodegradable polymer, is commercially available in the form of films used in flexible packaging such as candy wrappers, optically enhanced films, shrink films, and labels. These films offer a natural high surface energy and significant potential for modifications that provide desirable end-use properties and renewable raw material sourcing. Major development work with energy curing of flexo inks based on polyester acrylate or epoxidized oil acrylates is combining energy curing technology with biopolymer films. This approach is expected to reduce both VOC and $CO_2$ emissions.

## References

1. Golden, R., *RadTech Report*, 22, No. 4, July/August, p. 43 (2008).
2. Rix, B. A., and Bulluck, J. W., *RadTech Report*, 18, No. 6, November/December, p. 36 (2004).

3. Lopata, V. J., and Sidwell, D. R., *RadTech Report*, 17, No. 5, September/October, p. 32 (2003).

4. Bulluck, J. W., and Rix, B. A., U.S. Patent 7,291,657 to Texas Research International, Inc. (November 6, 2007).

5. Wood, K., *High Performance Composites*, 18, No. 6, November/December, p. 61 (2008).

6. Dworchak, M., UV/EB 2009 West, Los Angeles, February 17–19 (2009).

7. Saunders, C. B., et al., *Radiat. Phys. Chem.*, 46, No. 4–6, p. 91 (1995).

8. Nitshitsui, D. A., et al., *Nucl. Instrum. Meth. Phys. Res. B*, 265, p. 135 (2007).

9. Raghavan, J., *J. Composites A*, 40, p. 300 (2009).

10. Arcenaux, J. A., *RadTech Report*, 23, No. 1, January/February/March, p. 33 (2009).

11. Weissmann, P. T., *RadTech Report*, 23, No. 1, January/February/March, p. 23 (2009).

12. Martin, C., *RadTech Report*, 23, No. 1, January/February/March, p. 33 (2009).

13. Dworchak, M., UV/EB 2009 West, Los Angeles, February 17–19 (2009).

14. Rosenblum, M. R., Lin, S., and Chu, X., *RadTech Report*, 23, No. 3, July/August, p. 21 (2009).

15. Burton, K., *Paint & Coating Industry*, 25, No. 4, April, p. 44 (2009).

16. Krotine, F. T., and Ramsey, S. J. W., *Paint & Coating Industry*, 24, No. 11, November, p. 44 (2008).

17. Murphy, E. J., Cattron, W. W., and Kelly, J. J., *RadTech Report*, 23, No. 2, April/May/June (2009).

18. Oldenzijl, R., *RadTech Report*, 23, No. 3, July/August, p. 38 (2009).

19. Waldo, R., *RadTech Report*, 22, No. 4, July/August, p. 48 (2008).

20. Dworchak, M., and Gambino, C., UV/EB 2009 West, Los Angeles, February 17–19 (2009).

21. Sahara, R., RadTech Technology Expo and Conference, Chicago, May 4–7 (2008).

22. Harper, D. P., et al., SPE-ANTEC 2009 Conference, Chicago, June 22–24 (2009).

23. Grosemans, J., Kanouni, M., and Seecharan, A., *Converting*, 27, No. 7, July, p. 30 (2009).

# *Glossary*

**Abatement (technology):**  Various processes and methods (e.g., incinerators) designed to eliminate or reduce the amount of hazardous waste, environmental emissions, or effluents from a facility.

**Abrasion:**  The surface loss of a material due to frictional forces.

**Abrasion resistance:**  Reciprocal of abrasion loss.

**Absorbance:**  An index of the light absorbed by a medium compared to the light transmitted through it. Numerically it is the logarithm of the ratio of incident spectral irradiance to the transmitted spectral irradiance.

**Absorbed dose:**  The amount of energy absorbed per unit mass of the irradiated material.

**Absorptivity (or absorption coefficient):**  Absorbance per unit thickness of the medium.

**Accelerator:**  1. Equipment for the production of high-energy beams of elementary particles, such as electrons or protons, through application of electrical or magnetic forces. 2. Rubber compounding ingredient used in small amounts with a vulcanizing agent to increase the rate of vulcanization (cross-linking) of the base elastomer(s).

**Addition polymerization:**  A type of polymerization in which the small molecules (monomers) combine chemically to form polymer molecules without a by-product material being formed.

**Additive lamps:**  Arc or microwave medium-pressure mercury vapor UV lamps that have small amounts of different metal halides added to the mercury in the lamp. The halides emit their characteristic wavelengths in addition to mercury additions (this term is preferred over *doped lamps*).

**Adhesion:**  The state in which two surfaces are held together by interfacial forces, which may consist of valence forces or interlocking action or both.

**Adhesive:**  A material that, when applied, will cause two surfaces in contact with each other to adhere.

**Aging:**  The irreversible change of material properties after exposure to an environment for an interval of time (also used as the term for exposing the material to an environment for an interval of time).

**Alpha particle (symbol α):**  A positively charged particle emitted by certain radioactive materials; it is made up of two neutrons and two protons bound together, thus, it is identical to a helium atom. It is the least penetrating of the three most common types of radiation (alpha, beta, gamma) emitted by a radioactive material and can be stopped, for example, by a sheet of paper. It is not dangerous to

plants, animals, or humans unless the alpha-emitting substance has entered the body.

**Ambient temperature:** Room temperature or temperature in the surrounding area.

**Amorphous phase:** The part of a polymeric material that has no particular ordered arrangement in contrast to the crystalline phase, which is ordered. Semicrystalline polymers consist of different ratios of crystalline and amorphous phases.

**Angstrom (symbol Å):** Unit of length used for electromagnetic radiation, atomic, and their components, equaling $10^{-8}$ cm. It is used very seldom, since it has been replaced by a new unit, nanometer (nm), 1 nm = $10^{-9}$ m.

**Anionic polymerization:** A process proceeding by the addition of certain monomers to active center-bearing whole or partial negative charges.

**Annealing:** A heat treatment process directed at improving performance by removing stresses in the material formed during its fabrication. Typically, the part, sheet, or film is brought to a specific temperature for a definite period of time, and then cooled down slowly to ambient temperature.

**Antifoaming agent:** A chemical that is added to a liquid mix to prevent formation of foam, or added to the foam itself to break a foam already formed.

**Atomic mass unit:** one-twelfth the mass of a neutral atom of the most abundant isotope of carbon, $^{12}C$.

**Atomic number (symbol Z):** The number of protons in the nucleus of an atom, and also its positive charge. Each chemical element has a characteristic atomic number.

**Atomic weight:** The mass of an atom relative to other atoms. The atomic weight of an atom is approximately equal to the total number of protons and neutrons in its nucleus.

**Atomizing:** Dispersing solid or liquid particles into air.

**Back ionization:** Excessive buildup of charged particles limiting further deposition onto substrate.

**Backscatter:** Reflected or scattered radiation in the general direction of the source after it strikes matter (gas, liquid, or solid).

**Ballast:** An inductive transformer device that stabilizes the amount of current flowing through a bulb so that the power remains constant.

**Bandwidth:** The range of wavelengths between two identified limits.

**Beam:** A stream of particles or electromagnetic radiation, going into single direction.

**Beta particle (symbol β):** An elementary particle emitted from a nucleus during radioactive decay, with a single electrical charge and mass equal to 1/1,837 that of a proton. A negatively charged beta particle is identical to an electron. A positively charged beta particle is called a positron. Beta radiation can cause burns, and beta emitters are

harmful if they enter the human body. Beta particles are stopped easily by a thin sheet of metal.

**Betatron:** A doughnut-shaped accelerator in which electrons, traveling in an orbit of constant radius, are accelerated by a changing electromagnetic field. Energies up to 340 MeV have been attained in betatrons.

**Blowing agent:** Compounding ingredient used to produce gas by chemical or thermal action, or both, in manufacture of cellular or hollow articles.

***Bremsstrahlung*:** Electromagnetic radiation emitted by a fast-moving charged particle (usually electron), when it is slowed down (or accelerated) and deflected by the electric field surrounding a positively charged atomic nucleus. X-rays, produced in ordinary x-ray machines, are produced by this mechanism, and so are x-rays produced during irradiation of materials by electron beam. (In German, the term *bremsstrahlung* means "braking radiation.")

**Bulb:** A sealed quartz tube that contains mercury or other fill and is often fitted with electrical connections.

**Butadiene:** A gaseous hydrocarbon of the diolefin series. Can be polymerized into polybutadiene or copolymerized with styrene or acrylonitrile to produce SBR and NBR, respectively.

**Cable, electrical:** Either a stranded conductor with or without insulation, and other coverings (single-conductor cable), or a combination of conductors insulated from one another (multiple-conductor cable).

**Cable core:** The portion of an insulated cable lying under the protective covering or coverings.

**Cable sheath:** The protective covering applied to cables.

**Calender:** A precision machine equipped rolls with three or more heavy, internally heated or cooled (or both), revolving in opposite directions, used for continuously sheeting and plying up elastomeric compounds, and frictioning or coating with elastomeric compounds.

**Carbon black:** Finely divided carbon made by incomplete combustion or decomposition of natural gas or petroleum-based oils in different types of equipment. According to the process and raw material used, it can be furnace (e.g., HAF), thermal (e.g., MT), or channel carbon black (e.g., EPC), each having different characteristics, such as particle size, structure, and morphology. The addition of different types of carbon blacks to rubber compounds results in different processing behavior and vulcanizate properties.

**Cathode rays:** A stream of electrons emitted by a cathode, or negative electrode, of a gas-discharge tube or by a hot filament in a vacuum tube, such as a television tube.

**Cationic polymerization:** A process in which the active end of the growing polymer is a positive ion.

**Chafer strip:** A strip of rubber-coated fabric partially covering the bead assembly of a tire and extending above the rim line. Its function is the chafing of the bead on the rim.

**Channel black:** A form of carbon black produced from natural gas by the channel process.

**Chlorosulfonated polyethylene:** A product obtained by treatment of polyethylene by chlorine and sulfur dioxide. It is an elastomer highly resistant to chemicals and ozone.

**Cold mirror:** A reflector that is coated by a dichroic material that absorbs or passes wavelengths in the infrared region while reflecting those in the UV range.

**Composite:** In polymer technology a combination of a polymeric matrix and a reinforcing fiber with properties that the component materials do not have. The most common matrix resins are unsaturated thermosetting polyesters and epoxies, and reinforcing fibers are glass, carbon, and aramid fibers. The reinforcing fibers may be continuous or discontinuous. Some matrix resins are thermoplastics.

**Compound (elastomeric):** An intimate mixture of a polymer (or polymers) with all the ingredients necessary for the finished article.

**Compression molding:** A fabrication method in which a polymeric material, mostly a thermoset (a plastic or an elastomer), is compressed in a heated mold for a specific period of time.

**Compression set:** The residual deformation of a material after removal of the compressive stress.

**COPA:** Copolyamide (thermoplastic elastomer).

**COPE:** Copolyester (thermoplastic elastomer).

**Copolymer:** A polymeric material formed by the reaction of two or more monomers.

**Crystallinity, crystallization:** Orientation of the disordered long-chain molecules into repeated patterns.

**Cure (curing):** 1. Polymerization or cross-linking (or both) by radiation (UV or EB). 2. Cross-linking or vulcanization of elastomeric materials.

**Cyclotron:** A particle accelerator in which charged particles receive repeated synchronized accelerations by an electrical field as the particles spiral outward from their source. The particles are kept in the spiral by a powerful magnetic field.

**Damping:** The dissipation of energy with time or distance.

**Degradation:** Deterioration, usually in the sense of a physical or chemical process, rather than a mechanical one.

**Dichroic:** Exhibiting significantly different reflection or transmission in two different wavelength ranges.

**Dichroic reflector:** A reflector having reduced reflectance to long wavelengths (IR radiation); also called "cold mirror."

**Dielectric constant:** That property of a dielectric (insulating material) that determines the electrostatic energy stored per unit volume for unit potential gradient.

**Dielectric loss angle (symbol δ):** An angle between the vector for the amplitude of the total current and that for the amplitude of the charging

current. The tangent of this angle (tan δ) is the loss tangent, a direct measure of the dielectric loss.

**Dielectric strength:** The voltage that an insulating material can withstand before breakdown occurs, usually expressed as voltage gradient (volts per mil or mm).

**Diffuse:** A characteristic of a surface that reflects or scatters light in all directions.

**Doped lamp:** Term applied to a UV mercury lamp containing metal halide added to the mercury to alter the emission spectrum of the lamp (preferred term is *additive lamp*).

**Dose:** 1. In EB processing: the amount of energy absorbed per unit mass, unit 1 Gray (Gy) = 1 J/kg. 2. In UV processing: a common, but loosely used term for *irradiant energy density* or *flux density* at a surface of the medium of interest (unit $J/cm^2$).

**Durometer:** An instrument used for measuring hardness of an elastomeric or plastic material.

**Durometer hardness:** An arbitrary numerical value that indicates the resistance to indentation of the indentor point of a durometer.

**Dynamic exposure:** Exposure to a varying irradiance, such as when a lamp passes over a surface, or a surface passes under a lamp. In such a case, the energy density is the time integral of the irradiance profile.

**Dynamic properties:** Mechanical properties of polymeric materials exhibited under repeated cyclic deformation.

**Effective irradiance:** Radiant power, within a specified wavelength range, arriving at a surface per unit area (unit $J/cm^2$). If the wavelength range is understood, the term is shortened to *irradiance.*

**Einstein:** One mole of photons.

**Elasticity:** The property of a matter by virtue of which it tends to return to its original size and shape after removal of the stress causing deformation, such as stretching, compression, or torsion.

**Elastomer:** A macromolecular (polymeric) material that, at room temperature, is capable of recovering substantially in shape and size after removal of a deforming force.

**Electrodeless:** Referring to microwave-powered UV systems.

**Electromagnetic radiation:** Radiation consisting of associated and interacting electric and magnetic waves that travel at the speed of light (e.g., light, radio waves, gamma rays, x-rays); all can be transmitted through vacuum.

**Electromagnetic spectrum:** The full-wavelength range of electromagnetic radiation, including microwave, ultraviolet, visible, and infrared energy.

**Electron:** An elementary particle with a unit negative electric charge and a mass of 1/1,837 that of a proton. Electrons surround the positively charged nucleus of an atom and determine the chemical properties of the atom.

**Electronvolt (eV):** The amount of kinetic energy gained by an electron when it is accelerated through an electric potential difference of 1 volt. It is equivalent to $1.603 \times 10^{-12}$ erg. It is a unit of energy, or work, not of voltage.

**Elongation:** Extension of a body produced by a tensile stress.

**Elongation, ultimate:** The elongation at the time of rupture.

**Emission spectrum:** Radiation from an atom in an excited state, usually displayed as radiant power vs. wavelength. Each atom or molecule has a unique spectrum. The spectra can be observed as narrow line emission (atomic emission spectra) or as quasi-continuous emissions (molecular emission spectra). A mercury plasma emits both line spectra and continuous spectra simultaneously.

**Energy density:** Amount of radiant energy arriving at a surface per unit of area, commonly expressed in $J/cm^2$ or $mJ/cm^2$. It is an integral of irradiance over time.

**Extrusion:** A process in which heated or unheated polymeric material (plastic or elastomer) is forced through a shaping orifice (die) in one continuous shape, as in film, sheet, slab, profile, pipe, coating, etc.

**Fatigue, dynamic:** The deterioration of a material by a repeated deformation.

**Filament winding:** A process to produce a composite part from a continuous fiber impregnated by a matrix resin by winding it onto a rotating or stationary mandrel.

**Fluence:** The time integral of fluence rate ($J/m^2$ or $J/cm^2$). For a parallel and perpendicularly incident beam, not scattered or reflected, *energy density* and *fluence* become identical.

**Fluidization:** The process of suspending powder particles using compressed air, creating a fluid mixture of air and powder.

**Flux (radiant flux):** The flow of photons (in einstein/second).

**Free radical:** A reactive species having an unpaired electron that initiates a reaction with a double bond, for example, in acrylate polymerization. It is produced from its stable paired state by energy absorption.

**Free radical polymerization:** A process with a complex mechanism of initiation, propagation, and termination, of which the propagation and termination steps are typically very fast.

**Frequency:** The number of times a periodic wavelength cycle occurs in 1 s; the unit of measurement is hertz (Hz).

**Frictioning:** Process of impregnating woven fabric with rubber compound using a calender whose rolls rotate at different surface speeds.

**Furnace black:** A carbon black obtained by incomplete burning of natural gas or petroleum oil, or both in a large furnace.

**Gamma rays (symbol γ):** High-energy, short-wavelength electromagnetic radiation. Gamma radiation frequently accompanies alpha and beta emissions and always accompanies nuclear fission. Gamma rays are very penetrating and are best stopped or shielded against

by dense materials, such as lead or depleted uranium. Gamma rays are similar to x-rays, but are usually more energetic and are nuclear in origin.

**Gel:** A semisolid system consisting of a network of solid aggregates in which liquid is held.

**Glass transition (temperature), $T_g$:** The temperature at which the amorphous portion of a semicrystalline solid changes from its glassy state, becoming soft and flexible (rubbery); not to be confused with melting temperature.

**Graft copolymer:** A copolymer in which chains of one polymer are attached to chains of a previously formed polymer or copolymer in such a way that the junction points have three or more chains attached.

**Gray (Gy):** SI unit of radiation-absorbed dose, equals 1 J/kg; it has replaced the older unit, *rad*, which is 100 ergs/g (or 0.01 J/kg).

**Ground state:** The state of nucleus, atom, molecule, or any other particle at its lowest (normal) energy level.

**Gum (compound):** Unfilled elastomeric compound containing only ingredients necessary for a sufficient cross-linking.

**HAF (high abrasion furnace black):** Highly reinforcing furnace carbon black increasing resistance of a rubber compound to abrasion.

**Heat aging:** Exposure of polymeric materials under specified conditions (temperature, time, presence or absence of air or oxygen, etc.), then testing them in stress-strain and hardness, determining the change of properties in comparison to the original (unaged materials).

**Hysteresis:** Energy loss, the difference between the work output in a cycle of extension and retraction.

**Impact resistance:** Resistance to fracture under shock force.

**Intensity:** A generic term, with a variety of meanings, frequently used to mean *irradiance*, which is the correct and preferred term.

**Interpenetrating network (IPN):** A combination of two polymers into a stable interpenetrating network. In a true IPN each polymer is cross-linked to itself, but not to the other, and the two polymers interpenetrate each other. In a semi-IPN, only one of the polymers is cross-linked; the other is linear and by itself would be a thermoplastic. The purpose of producing IPN is to improve strength, stiffness, and chemical resistance of certain polymeric systems.

**Ionization:** The process of adding one or more electrons to, or removing one or more electrons from, atoms or molecules, thereby creating ions. High temperatures, electric discharges, nuclear radiation, or high-energy electrons can cause ionization.

**Ionizing radiation:** Any radiation displacing electrons from atoms or molecules (e.g., alpha, beta, and gamma radiation). Ionizing radiation may produce severe skin and tissue damage.

**Irradiance:** Radiant power arriving at a surface from all forward angles, per unit area, expressed in watts per unit area ($W/cm^2$ or $mW/cm^2$).

**Irradiance profile:**  The irradiance pattern of a lamp or, in the case of dynamic exposure, the varying irradiance at a point on a surface that passes through the field of illumination of a lamp or lamps; irradiance vs. time.

**Irradiation:**  Application of radiation to an object.

**Irradiator (lamp head):**  Assembly or fixture that is a sheet metal housing containing the UV bulb, reflector, shutter, magnetrons, or screens; it may also include a blower.

**Isotope:**  One or more atoms with the same atomic number (the same chemical element) but with different atomic weights. The nuclei of isotopes have the same number of protons but a different number of neutrons. Thus, $^{12}C$, $^{13}C$, and $^{14}C$ are isotopes of the same element, carbon, the superscripts denoting their differing mass numbers or approximate atomic weights. Isotopes usually have very nearly the same chemical properties, but somewhat different physical properties.

**Joule:**  A unit of work or energy (N-m), abbreviated as J. It is a time integral of power.

**Latex:**  An aqueous colloidal emulsion of an elastomer (natural or synthetic) or a plastic. It generally refers to the emulsion obtained from a tree or plant or produced by emulsion polymerization.

**Lethal dose:**  A dose of ionizing radiation sufficient to cause death. Median lethal dose (MLD or LD50) is the dose required to kill within a specified period of time (usually 30 days) half of the individuals in a large group or organisms similarly exposed. The LD50/30 for man is 400 to 500 rads (4–5 Gy).

**Linac:**  Short for linear accelerator.

**Linear accelerator:**  A long straight tube (or series of tubes) in which charged particles (ordinarily electrons or protons) gain in energy by the action of oscillating electromagnetic fields.

**Line emission:**  Narrow lines of emission from an atom in the excited state; the "spikes" observed in spectrometry.

**Magnetron:**  Component contained inside a microwave-powered lamp head that converts high-voltage electrical input into microwave energy at 2,450 MHz.

**MDF:**  Medium-density fiberboard. A composite panel product manufactured from wood fibers and synthetic resin binders bonded together under heat and pressure; the fibers and resin form a homogeneous board with consistent properties in each direction.

**Micrometer (µm):**  Unit of length equal to 1 millionth of a meter; replaces an older term, *micron*.

**Microwave:**  Designating the part of the electromagnetic spectrum associated with the larger infrared waves and the shorter radio waves, between 1 and 10 mm.

**Modulus:**  The ratio of stress to strain. In the physical testing of rubber, it is the force in pounds per square inch (psi) of original area or

pascals (Pa) related to original area to produce a state percentage elongation.

**Monochromatic:** Light radiated from a source that is concentrated in only a very narrow wavelength range (bandwidth). This may be accomplished either by filters or by narrow-band emission.

**Monochromator:** An instrument that separates incoming radiant energy into its component wavelengths for measurement.

**Monomer:** A low-molecular-mass substance consisting of molecules capable of reacting with like and unlike molecules to form a polymer.

**Nanometer:** Unit of length commonly used to define wavelength of light, particularly in the ultraviolet and visible ranges of the electromagnetic spectrum. It equals $10^{-9}$ m or $10^{-3}$ µm or 10 Å.

**Neutron:** An uncharged elementary particle with a mass slightly greater than that of the proton, and found in the nucleus of every atom heavier than hydrogen (atomic weight = 1).

**Ozone (formula O$_3$):** An allotropic form of oxygen, produced by the action of electric discharges or of a certain ultraviolet wavelength of light on oxygen. It is a gas with a characteristic odor, and is a powerful oxidizing agent.

**Peak irradiance:** The intense peak of focused power under a lamp, the maximum point of the irradiance profile. The unit of measurement is W/cm$^2$.

**Permanent set:** The amount by which an elastic material fails to return to its original form after deformation.

**Photon:** The carrier of a quantum of electromagnetic energy. Photons have an effective momentum but no mass or electrical charge.

**phr:** Abbreviation used in formulation of elastomeric compounds indicating parts in mass units per hundred parts of rubber.

**Ply:** Most commonly applies to a layer of rubber-coated fabric (as in tire or belt design). Polychromatic or polychromic consisting of many wavelengths.

**Polymer:** A macromolecular material formed by the chemical combination of monomers having either the same or different chemical composition.

**Polymerization:** A chemical reaction in which the molecules of monomers are linked together to form large molecules whose molecular mass is a multiple of that of the original substance. When two or more monomers are involved, the process is called copolymerization or heteropolymerization.

**Power (of a UV lamp):** Operating power of a tubular lamp is described in watts/inch (W/in) or watts per cm (W/cm). It is derived by simply dividing the electric power by the effective length of the lamp.

**Proton:** An elementary particle with a single positive electrical charge and a mass approximately 1,837 times that of an electron; the nucleus of the ordinary, or light hydrogen, atom. Protons are constituents of all

nuclei. The atomic number (Z) of an atom is equal to the number of protons in its nucleus.

**Quantum yield:** A measure of a photochemical efficiency of a photochemical reaction, expressed as the ratio of the number of chemical events per unit time to the number of photons absorbed per unit time; it is a unitless quantity.

**Rad (acronym for *radiation-absorbed dose*):** The original basic unit of absorbed dose of ionizing radiation; one rad equals 100 ergs of radiation energy per gram of absorbing material. This unit has been replaced by the gray (Gy).

**Radiachromic:** Exhibiting a change of color or optical density with exposure to UV or EB radiation. These changes can be correlated to the amount of exposure.

**Radiant energy:** Energy transfer, expressed in joules or watt-seconds (1 J = 1 W).

**Radiant power:** Rate of energy transfer, expressed in watts or joules per second (1 W = 1 J/z).

**Radiation illness:** An acute organic disorder that follows exposure to relatively severe doses of ionizing radiation. It is characterized by nausea, vomiting, diarrhea, blood cell changes, and in later stages, hemorrhage and loss of hair.

**Radiometer:** An instrument that senses irradiance incident on its sensor element and may incorporate either a thermal or photonic detector.

**Rem (acronym for *roentgen-equivalent man*):** The unit of dose of ionizing radiation that produces the same biological effect as a unit of absorbed dose of ordinary x-rays.

**Resilience:** The ratio of energy output to energy input in a rapid (or instantaneous) full recovery of a deformed specimen.

**Responsivity (spectral sensitivity):** The response or sensitivity of any system in terms of incident wavelength. In radiometry, it is the output of a device vs. wavelength.

**RF (radio frequency):** Any frequency between normally audible sound waves and the infrared portion of the spectrum lying between 10 kHz and $10^6$ MHz.

**RoHS (Restriction of Hazardous Substances) Directive:** Restricts the use of certain dangerous substances in electrical and electronic equipment.

**Rubber:** A material that is capable of recovering from large deformations quickly and forcibly and can be, or already is, modified to a state in which it is essentially insoluble (but can swell) in boiling solvent such as benzene, methyl ethyl ketone, and ethanol-toluene azeotrope. A rubber in its modified state, free of diluents, retracts within 1 min to less than 1.5 times of its original length after being stretched at room temperature to twice its length and held for 1 min before release.

**SBS:** Styrene-butadiene-styrene block copolymer.

**SEBS:** Styrene-ethylene-butylene-styrene block copolymer.

**SEPS:** Styrene-ethylene-propylene-styrene block copolymer.

**Semicrystalline polymer:** A material consisting of a combination of crystalline and amorphous regions. Essentially, all common plastics and elastomers with the tendency to crystallize are semicrystalline. The degree of crystallization depends on the structure of the polymer and the conditions of fabrication.

**Spectral absorbance (absorbance spectrum):** Absorbance described as function of wavelength.

**Spectral irradiance:** Irradiance at a given wavelength per unit wavelength integral, expressed in $W/cm^2/nm$; measured usually with a spectroradiometer.

**Spectral output:** The radiant output of a lamp vs. wavelength. It is displayed in a variety of ways, the most common being the integration of the energy over 10 nm bands, which reduces the difficulty of quantifying the effects of line emission spectra.

**Spectroradiometer:** An instrument that combines the functions of a radiometer and a monochromator to measure irradiance in finely divided bands.

**Static exposure:** Exposure to a constant irradiance for a controlled period of time.

**Sulfur:** Chief vulcanizing agent for many elastomers, particularly those based entirely or part on butadiene or isoprene.

**Tack (or building tack):** A property of an elastomer or rubber compounds that causes two layers of compound that have been pressed together to adhere firmly in the areas of contact. It is very important for building tires or other laminated structures.

**Target:** Material subjected to particle bombardment (as in accelerator) or irradiation (as in reactor) in order to induce nuclear reaction.

**Tentering:** A continuous process for drying cloth while held under tension to remove wrinkles and give a smooth surface, also for orienting polymeric films or sheets in the transverse (cross-machine) direction.

**Tentering frame:** A machine used to stretch textiles and polymeric films and sheets.

**Terpolymer:** A copolymer made from three different polymers.

**Thermal black:** Soft carbon black formed by the decomposition of natural gas (e.g., MT, medium thermal black). It has little stiffening effect, but imparts toughness, resilience, good resistance to tearing, and fair abrasion resistance.

**Thermoplastic:** A material capable of being repeatedly softened by increase of temperature and hardened by decrease of temperature (*see* plastics).

**Thermoplastic elastomer (TPE):** A polymeric material that is elastic at ambient or moderately elevated or lowered temperature that can be

processed and recycled as a thermoplastic (i.e., by melt processing). The processing and service temperatures depend on the chemical nature of the material.

**Tire, pneumatic:** A tire casing (consisting of cord fabric), tread, sidewalls, and bead with or without an inner tube, capable of being inflated with a gas.

**TPU:** Thermoplastic polyurethane (thermoplastic elastomer)

**Vulcanization:** An irreversible process during which an elastomeric compound, through a change in its chemical structure (e.g., cross-linking), becomes more elastic and more resistant to swelling by organic liquids, and elastic properties are conferred, improved, or extended over a greater range of temperature.

**Watt:** The unit of power equal to the work done at the rate of 1 joule per second, or the power produced by a current of 1 ampere across a potential difference of 1 volt; 1/746 horsepower; abbreviated W, a smaller unit is a *milliwatt* (mW). In optics, it is a measure of radiant or irradiant power.

**Waveguide:** A device directing microwaves toward the bulb in microwave-powered UV systems.

**Wavelength:** A fundamental descriptor of electromagnetic energy, including light. It is the distance between corresponding points of a propagated wave, frequently using the symbol $\lambda$ (lambda). It is the velocity of light divided by the equivalent frequency of oscillation associated with a photon. The unit of measurement is a *nanometer* ($10^{-9}$ m).

**X-ray:** A penetrating electromagnetic radiation emitted when the inner orbital electrons of an excited atom return to their normal state. X-rays are usually nonnuclear in origin and are generated by bombarding a metallic target with high-speed electrons.

**Z:** The symbol for atomic number.

# *Appendix I: Bibliography*

Below is a list of books that may provide additional and often detailed information on various topics in radiation science and technology. They are listed chronologically, starting with the most recent publications. Efforts were made to make this list as complete as possible.

Glöckner, P., Jung, T., Struck, S., and Studer, K., *Radiation Curing: Coatings and Printing Inks (European Tech Files)*, Vincentz Network, Hannover (2008).

Schwalm, R., *UV Coatings, Basics, Recent Developments and New Applications*, Elsevier, Amsterdam (2007).

*UV Technology: Practical Guide for All Printing Processes*, Berufgennosenschaft Druck- und Papierverarbeitung, Wiesbaden, Germany (2007).

*RadTech Printer's Guide*, RadTech International North America, Bethesda, MD, www. radtech.org.

Läuppi, U. V., EB/UV/γ terms (*English-German and German-English Dictionary*), Vincentz Network, Hannover (2003).

Drobny, J. G., *Radiation Technology for Polymers*, CRC Press, Boca Raton, FL (2003).

Talbert, R. (Ed.), *UV Powder Coating Application Guide*, RadTech International North America, Chevy Chase, MD (2002).

Koleske, J. V., *Radiation Curing of Coatings*, ASTM International, West Conshohocken, PA (2002).

Dietliker, K., *Compilation of Initiators Commercially Available for UV Today*, SITA Technology Ltd., Edinburgh and London (2002).

*ASTM Standards Related to Testing of Radiation-Cured Coatings*, ASTM International, Conshohocken, PA (2001). On CD-ROM.

Davidson, R. S., *Exploring the Science, Technology and Applications of U.V. and E.B.*, SITA Technology Ltd., London (1999).

Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., and Berejka, A., *UV & EB Technology & Equipment*, Vol. I., John Wiley & Sons Ltd., Chichester and SITA Technology, Ltd., London (1998).

Clough, R. L., and Shallaby, S. W. (Eds.), *Irradiation of Polymers, Fundamentals and Technological Applications*, ACS Symposium Series 620, American Chemical Society, Washington, DC (1996).

Garrat, P. G., *Strahlenhärtung*, Curt R. Vincentz Verlag, Hannover, Germany (1996).

Fouassier, J.-P., *Photoinitiation, Photopolymerization, and Photocuring; Fundamentals and Applications*, Hanser Publishers, Munich (1995).

Rechel, C. (Ed.), *UV/EB Curing Primer: Inks, Coatings and Adhesives*, RadTech International, North America, Northbrook, IL (1995).

Singh, A., and Silverman, J. (Eds.), *Radiation Processing of Polymers*, Carl Hanser Verlag, Munich (1992).

Fouassier, J.-P., and Rabek, J. F. (Eds.), *Radiation Curing in Polymer Science and Technology*, Vols. I–IV, Elsevier, London (1993).

Pappas, S. P. (Ed.), *Radiation Curing Science and Technology*, Plenum Press, New York (1992).

Oldring, P. K. T. (Ed.), *Chemistry and Technology of UV and EB Formulations for Coatings, Inks and Paints*, Vols. 1–5, SITA Technology Ltd., London (1991).

Clegg, D. W., and Collyer, A. A. (Eds.), *Irradiation Effects on Polymers*, Elsevier, London (1991).

Hoyle, C. E., and Kinstle, J. F. (Eds.), *Radiation Curing of Polymeric Materials*, ACS Symposium Series 417, American Chemical Society, Washington, DC (1990).

Farhataziz, M. A. J., *Radiation Chemistry*, VCH, Weinheim (1990).

Allen, N. S. (Ed.), *Photopolymerization and Photoimaging Science and Technology*, Elsevier, Essex (1989).

Reiser, A., *Photoreactive Polymers: The Science and Technology of Resists*, John Wiley & Sons, New York (1989).

McLaughlin, W. L., Chadwick, K. H., McDonald, J. C., and Miller, A., *Dosimetry for Radiation Processing*, Taylor & Francis, London (1989).

Bly, J. H., *Electron Beam Processing*, International Information Associates, Yardley, PA (1988).

Randell, D. R. (Ed.), *Radiation Curing of Polymers*, Royal Society of Chemistry, London (1987).

Humphries, S., Jr., *Principles of Charged Particle Acceleration*, John Wiley & Sons, New York (1986).

Guillet, J., *Polymer Photophysics and Photochemistry*, Cambridge University Press, Cambridge (1985).

Bradley, R., *Radiation Technology Handbook*, Marcel Dekker, New York (1984).

Pappas, S. P. (Ed.), *UV Curing: Science and Technology*, Vol. 2, Technology Marketing Corp., Norwalk, CT (1984).

Schiller, S., et al., *Electron Beam Technology*, John Wiley & Sons, London (1983).

Raffey, C. G., *Photopolymerization of Surface Coatings*, Wiley-Interscience, New York (1982).

Pappas, S. P. (Ed.), *UV Curing: Science and Technology*, Vol. 1, Technology Marketing Corp., Norwalk, CT (1978).

Kase, K. R., and Nelson, W. R., *Concepts of Radiation Chemistry*, Pergamon Press, New York (1978).

Dole, M. (Ed.), *Radiation Chemistry of Macromolecules*, Academic Press, New York (1974).

Wilson, J. E., *Radiation Chemistry of Monomers, Polymers and Plastics*, Marcel Dekker, New York (1974).

Dole, M. (Ed.), *Radiation Chemistry of Macromolecules*, Vols. 1 and 2, Academic Press, New York (1972, 1973).

Holm, N. W., and Berry, R. J., *Manual on Radiation Dosimetry*, Marcel Dekker, New York (1970).

Chapiro, A., *Radiation Chemistry of Polymeric Systems*, Wiley-Interscience, New York (1962).

Charlesby, A., *Atomic Radiation and Polymers*, Academic Press, London (1960).

# *Appendix II: Major Equipment Manufacturers*

**TABLE II.1**

UV Equipment Manufacturers

| Manufacturer | Web Page | Products |
|---|---|---|
| American Ultraviolet Company | www.americanultraviolet.com | UV equipment, UV light sources, spot curing equipment, ballasts |
| Ayottte Technology, Inc. | www.americanovens.com | UV light sources |
| ClearTech Industries, Inc. | www.cleartech.ca | UV equipment, UV light sources, measuring equipment |
| DYMAX Corporation | www.dymax.com | UV equipment, UV light sources, measuring equipment |
| EIT Instrument Markets | www.eitinc.com | UV equipment, testing equipment |
| Energy Sciences, Inc., EYE Ultraviolet | www.ebeam.com | UV equipment, UV light sources |
| EXFO Life Sciences & Industrial Division | www.company7.com/exfo | UV equipment, UV light sources, measuring equipment |
| Fusion UV Systems | www.fusionuv.com | UV equipment, UV light sources |
| Hamamatsu Corporation | www.ushamamatsu.com | Equipment, UV light sources |
| Hanovia | www.hanovia-uv.com | UV equipment, UV light sources |
| Heraeus GmbH | www.heraeus-noblelight.com | UV equipment, UV light sources (standard and excimer), ballasts |
| Hologenix, Inc. | www.hologenix.com | UV equipment, UV light sources, spot and small area curing systems LED illumination |
| Honle UV America, Inc. | www.honleuv.com | UV equipment, UV light sources, testing equipment |
| IST Metz GmbH | www.ist-uv.com | UV equipment, UV light sources, testing equipment |
| Nicollet Technologies | www.nictec.com | UV equipment, gas discharge lamps, ballasts |
| Nordson UV | www.nordsonuv.com | UV equipment, UV light sources, ballasts Power supplies |
| OnLine Energy, Inc. | www.onlineenergy.com | UV equipment, UV light sources |
| Prime UV-IR | www.primeuv.com | UV equipment, UV light sources, testing equipment |

*(continued)*

**TABLE II.1 (CONTINUED)**

UV Equipment Manufacturers

| Manufacturer | Web Page | Products |
|---|---|---|
| Ultraviolet Connection | www.ultravioletsystems.com | UV equipment, UV light sources, measuring equipment |
| Ushio America, Inc. | www.ushiosemi.com | UV equipment, UV light sources, UV excimer lamps |
| UVEXS, Inc. | www.uvexs.com | UV equipment, measuring and testing equipment |
| UV Robotics LLC | www.uvrobotics.com | UV equipment and light sources, robotic systems with UV lamps |
| Xenon Corporation | www.xenon-corp.com | UV equipment, UV light sources |

**TABLE II.2**

EB Equipment Manufacturers

| Manufacturer | Web Page | Products |
|---|---|---|
| Advanced Electron Beams, Inc. | www.advancedelectronbeams.com | Low-voltage electron beam equipment |
| Cross-linking AB | www.crosslinking.com | Electron beam equipment, dose measuring equipment |
| Energy Sciences, Inc. | www.ebeam.com | Electron beam equipment |
| IBA | www.iba-worldwide.com | Electron beam and x-ray irradiation equipment |
| Nissin Electric | www.nissin.co.jp | Electron beam and x-ray irradiation equipment, several designs |
| PCT Engineered Systems | www.teampct.com | Low- to medium-voltage electron beam equipment |
| Steigerwald Strahltechnik GmbH | www.steigerwald-eb.de | EB equipment mainly for welding, drilling, and research |
| Ushio America | www.ushiosemi.com | Low-voltage EB equipment |

# *Appendix III: Standard Dosimetry Tests*

**ASTM E170:** Standard Terminology Relating to Radiation Measurements and Dosimetry

**ASTM E668:** Standard Practice for Application of Thermoluminiscence-Dosimetry (TLD) Systems for Determining Absorbed Dose in Radiation-Hardness Testing of Electronic Devices

**ASTM E1026:** Standard Practice for Using the Fricke Reference-Standard Dosimetry System

**ISO/ASTM 51204:** Standard Practice for Dosimetry in Gamma Irradiation Facilities for Food Processing

**ISO/ASTM 51261:** Standard Guide for Selection and Calibration of Dosimetry Systems for Radiation Processing

**ISO/ASTM 51275:** Standard Practice for Use of Radiochromic Film Dosimetry System

**ISO/ASTM 51276:** Standard Practice for Use of Polymethylmethacrylate Dosimetry System

**ISO/ASTM 51707:** Standard Guide for Estimating Uncertainties in Dosimetry for Radiation Processing

## Other Resources for Dosimetry

*Guidance Notes for Dosimetric Aspects of Dose Setting Methods*, Panel on Gamma and Electron Irradiation, London (1997).

*Guide to UV Measurements: UV Technology, Radiometry and Measurements for Industrial UV Curing*, RadTech International North America, Chevy Chase, MD, www.radtech.org. CD ROM.

Sharpe, P., and Miller, A., *Guidelines for the Calibration of Dosimeters for Use in Radiation Processing*, National Physical Laboratory, Teddington, UK (1999).

## Other Tests for Radiation-Cured Coatings

*ASTM Standards Related to Testing of Radiation-Cured Coatings*, ASTM International, West Conshohocken, PA (2001). CD-ROM.

# *Appendix IV: Major Suppliers of Raw Materials for UV/EB Curing*

| Supplier | Web Page |
|---|---|
| Aceto | www.aceto.com |
| BASF | www.basf.com/coatingsrawmaterials |
| Bayer Material Science | www.bayermaterialsciencenafta.com |
| Bomar Specialties Co. | www.bomarspecialties.com |
| Chemidex LLC | www.chemidex.com |
| Ciba Specialty Chemicals | www.cibasc.com |
| Cognis Corporation | www.cognis.com |
| Cytec | www.cytec.com/spacialty-chemicals/radcure/php |
| Dupont Powder Coatings | www.dupont.com |
| Lubrizol Advanced Materials | www.lubrizol/coatings.com |
| Nicollet Technologies Corp. | www.nictec.com |
| Rahn AG | www.rahn-group.com |
| Rahn USA | www.rahn-group |
| R.M. Ferguson & Co., Inc | www.rmferguson.com |
| San Esters Corp | www.sanesters.com |
| Sartomer | www.sartomer.com |
| Sun Chemical Ink (GPI) | www.sunchemicalink.com |
| Velsicol Chemical Corporation | www.velsicol.com |

# Appendix V: The Twelve Principles of Green Chemistry[*]

1. It is better to prevent waste than to treat or clean up waste after it is formed.

2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.

5. The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary whenever possible and innocuous when used.

6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

7. A raw material feedstock should be renewable rather than depleting whenever technically and economically practical.

8. Unnecessary derivatization (blocking group, protection, and deprotection, temporary modification of physical and chemical processes) should be avoided whenever possible.

9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

11. Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.

12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

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[*] Anastas, P. T., and Warner, J. C., *Green Chemistry Theory and Practice*, Oxford University Press, p. 30 (1998). (With permission from Oxford University Press.)

# *Index*

**Materials Science**

SECOND EDITION

# Radiation Technology for Polymers

Jiri George Drobny

The first edition of *Radiation Technology for Polymers* set the standard as a valuable, time-saving resource offering systematic fundamental information about industrial radiation technologies. Raising the bar even further, *Radiation Technology for Polymers, Second Edition* explores emerging applications of ultraviolet (UV) and electron beam (EB) radiation to polymer processing, detailing significant changes in the field since the first publication.

**PRESENTS IMPORTANT NEW PROCESSING AND ENGINEERING DATA FROM SELECTED COMMERCIAL PRODUCTS**

Since the publication of the previous edition, many technological developments have taken place, new applications and products have been developed and commercialized, and some already established ones have been discontinued. This book updates changes, trends, and general issues in radiation technology. It presents vital, cutting-edge information to aid further reduction of volatile organic compounds and toxic substances in the environment, develop alternative sources of energy, and harness energy in both medical and industrial applications.

The author considers novel uses of UV/EB technology in:

- Equipment and instrumentation developments in automotive, electronics, and wood-processing industries
- Applications used in waterborne coatings and adhesives, film modifications, high-performance coatings, and inkjet technology
- Processing of coatings, paints, inks, and adhesives, and thermoplastics as well as elastomers in film, sheet, and other forms

This reference discusses new uses for UV and EB irradiation, the response of polymers to irradiation, and tests related to dosimetry and radiometry, as well as safety and hygiene. It is also fortified with new problems and worked solutions, in addition to useful figures and tables, and appendices with supplementary information on equipment manufacturers, raw materials suppliers, and principles of green chemistry and sustainability.